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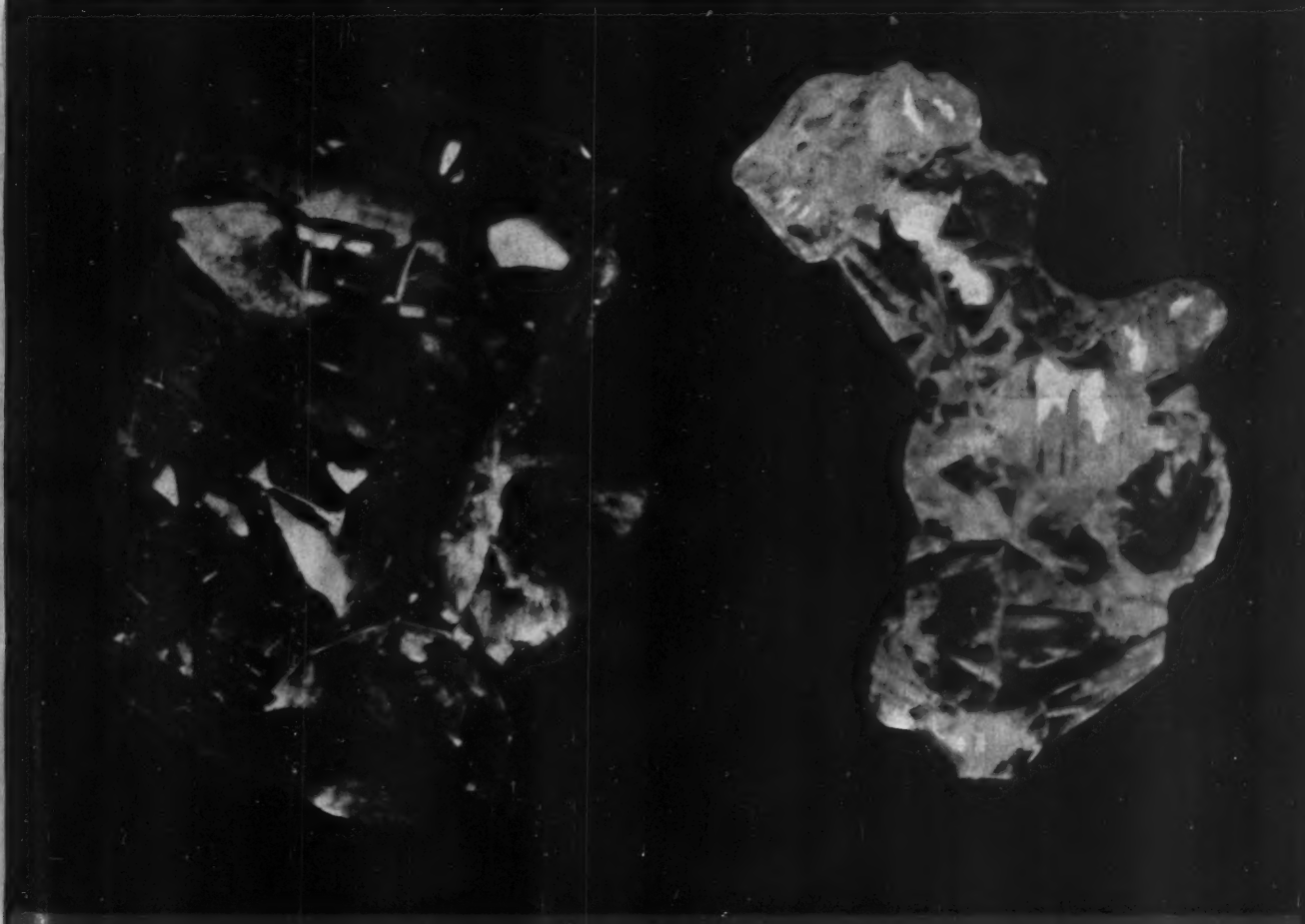

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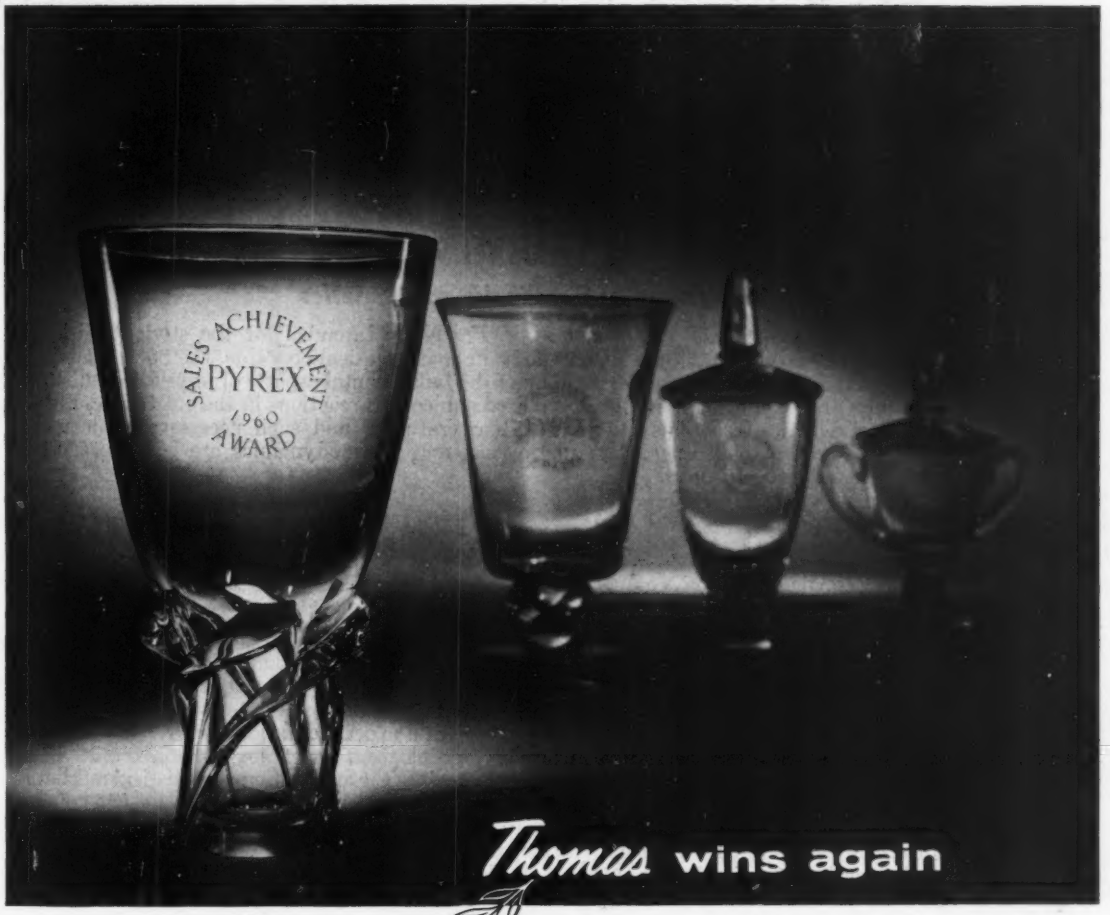

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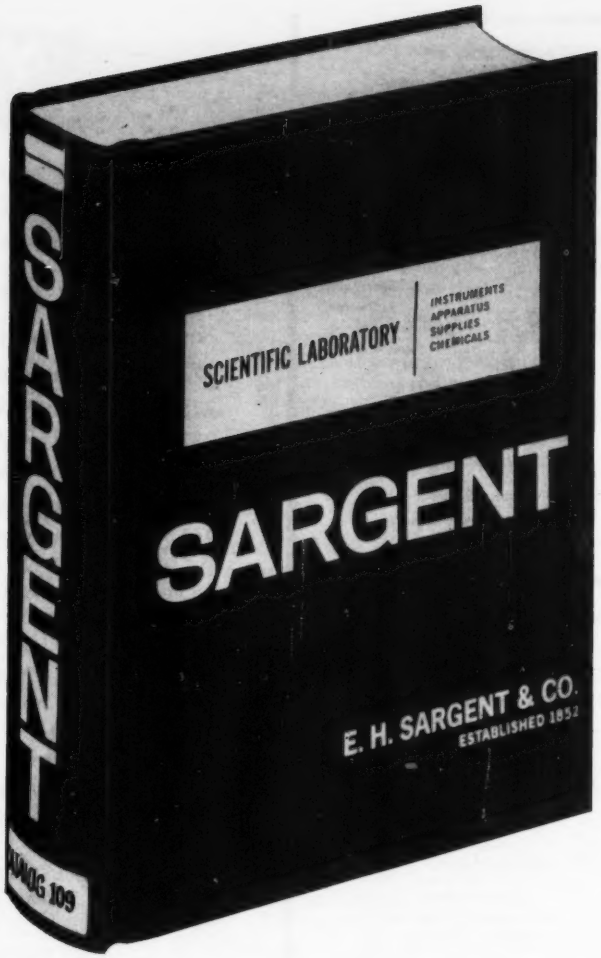

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13. Nuclear Radiation Electronic Gear (Continued)

Pulse Amplifiers

The amplifiers that have been described in the foregoing are intended for use with detectors that measure the total ionization produced by the nuclear radiation source, and their principal requirement is for very high amplification combined with stability, i.e., freedom from excessive drift and noise. When it is desired to count individual radioactive events, it is necessary to employ an amplifier with properties that are appropriate to the nature and frequency of the detector pulses, as well as to the type of information it is desired to obtain about the pulses.

The first requirement of a pulse amplifier is that it must be capable of accepting and passing signals with rapid rise times and short durations. A pulse is fed onto the grid of a vacuum tube by being applied to one plate of a capacitor, the other plate of which is connected both to the grid and, through a large resistor, to a grid bias voltage or to ground, as shown in Figure 11. If the pulse is thought of

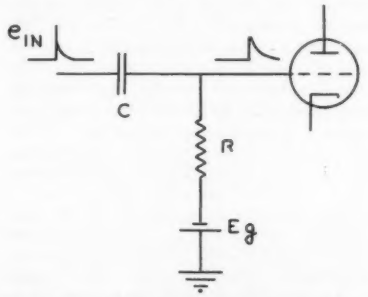

Figure 11. Pulses are fed into an amplifier through an RC circuit, the time constant of which determines the shape and height of the pulse that reaches the grid of the vacuum tube.

as a burst of electrons approaching the left-hand plate of the capacitor in the figure, it will be clear that a similar burst of electrons must be repelled from the right-hand plate. These electrons are repelled onto the grid of the vacuum tube, making it more negative, and thus the electron pulse has been transmitted through the capacitor as a negative-going signal on the grid. This charge, however, immediately begins to leak away through R, and the signal on the grid decays in magnitude. The rate of decay is governed by the product RxC, which is called the *time constant* of the circuit. If the time constant is extremely short (RC very small), all the electrons repelled from the right-hand plate of the condenser may leak away through R so quickly that no signal ever builds up on the grid of the vacuum tube. On the other hand, if RC is too large, the charge released by one pulse may still be on the grid when a second pulse comes in, and the amplifier will be unable to resolve individual pulses. In pulse amplifiers, the time constant of the input stage, as well as of subsequent stages, is usually in the range of 0.1 to 10 microseconds, this being a long enough time constant to permit a usable signal to be transmitted to the grid of the vacuum tube, yet short enough to permit the signal to decay substantially completely between pulses for most counting rates. (If C = 1 micromicrofarad and R = 1 megohm, $RC = 10^6$ ohms $X\ 10^{-12}$ farads = 10^{-6} seconds).

A pulse amplifier for use with a Geiger-Mueller detector can be a relatively simple instrument, for the detector pulses are large and fairly uniform in size, and their pulse height has no special significance. However, the reliability and signal-to-noise ratio of these amplifiers are markedly improved by the use of negative feedback and pulse-shaping circuitry. In the case of amplifiers for scintillation and proportional counters, these features are usually indispensable.

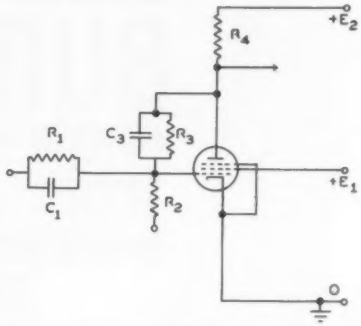

Figure 12. A negative feedback stabilized stage of amplification. The feedback of a portion of the output in opposition to the input takes place through R_3, C_3.

The use of *negative feedback* to stabilize the gain and improve the linearity of an amplifier is illustrated by the schematic diagram in Figure 12. If a negative-going signal is applied to the grid of the pentode shown in the Figure, the tube current will decrease. This causes the potential of the plate to become more positive (since $I\ X\ R_4 = E_4$ is reduced, the plate potential rises toward the supply voltage, E_2), and a positive-going signal is transmitted through C_3 and R_3 to the control grid, partially cancelling the primary negative-going signal. Thus, a portion of the output is fed back in opposition to the input, and the net output signal is smaller than it would be without the feedback. However, the new output is stabilized by this feedback arrangement,

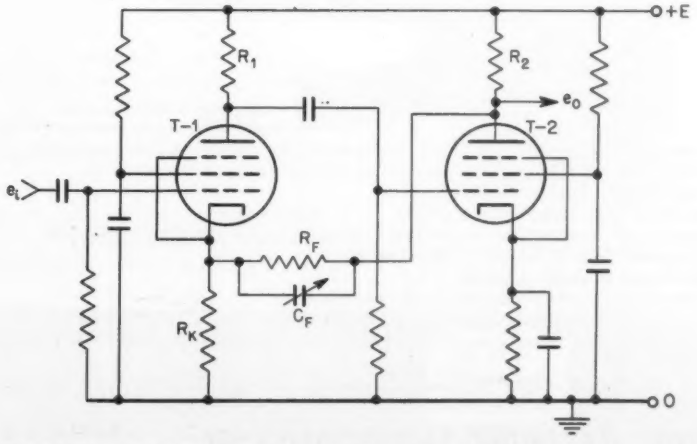

Figure 13. An example of a feedback loop, in which a fraction of the output of the second stage is fed back to the grid of the first stage.

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and can be made substantially independent of drifts and random fluctuations occurring in the characteristics of the vacuum tube.

When several stages of amplification are used, it is often effective to employ a *feedback loop*, such as is shown in simplified form in Figure 13. Here, a fraction of the amplified signal in the second stage is fed back in opposition to the primary signal in the first stage. A negative-going signal impressed on the grid of pentode *T-1* causes the tube current to decrease; this causes the potential of the plate of *T-1* to rise, and as a consequence a positive-going pulse is transmitted through the inter-stage coupling condenser to the grid of the second stage pentode, *T-2*. The current through this tube then increases, and the increased *IR*-drop in the plate resistor, R_2, causes the plate potential to decrease (become more negative relative to the supply voltage, E). This negative-going effect at the plate of *T-2* is transmitted through the feedback coupling circuit, R_F-C_F, to the cathode of *T-1*, causing it to feel a negative pulse. But driving the cathode negative is equivalent to making the grid positive relative to its cathode. Hence, the portion of the second stage output signal fed back to the first stage diminishes the original negative-going grid signal that is being amplified.

Pulse-Shaping

Pulse-shaping circuits are employed to modify the characteristics of the input signal so that they are better suited to the requirements of the amplifier than is the original pulse from the radiation detector. One such circuit is the *univibrator*, shown in schematic diagram in Figure 14. In this arrangement, one of the vacuum tubes is normally conducting, and the other is cut off. A suitable pulse applied to the cut-off tube causes the circuit to "flip over," i.e., the tube that was off comes on, and the one that was on goes off. This situation lasts only briefly, and then the circuit reverts to its original condition. Thus, a pulse applied to one tube of the pair can be translated into a differently-shaped pulse taken from a suitable place in the circuit of the other tube.

The principle of operation of the univibrator circuit can be understood relatively simply on the basis of the following qualitative considerations. The values of the various resistors and voltages in Figure 14 are chosen so that tube *T-1* is conducting, and tube T-*2* is cut off. The grid of tube *T-1*, although connected through R_2 to the +300 v source, is actually at about ground potential, for it picks up grid current, I_g, until $I_g x R_2$ is approximately equal to 300 v. (If I_g = 0.3 milliamperes, $I_g \times R_2 = 3 \times 10^{-4}$ amp X 10^6 ohm = 300 v). The current flowing from cathode to plate in tube *T-1* under these conditions is about 10 milliamperes, and since this makes the *IR*-drop in plate resistor R_1 equal to 200 v (10 ma × 20 Kohms), the plate potential of *T-1* is about +100 v. Resistors

(Continued on page A308)

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R_3 and R_4 serve, therefore, as a voltage divider circuit between the voltages of +100 at one end and −150 v at the other end. Thus, the potential of the grid of *T-2* is more positive than −150 v by the amount:

$$\frac{R_4}{R_3 + R_4}(250) = \frac{150}{375}(250) = 100 \text{ v}$$

That is, the grid of *T-2* is at −50 v relative to ground, and this is sufficiently negative to keep the tube from passing any current.

If, now, a positive-going signal is applied to the grid of *T-2* in sufficient magnitude to cause this tube to begin to conduct, the following *regenerative effect* sets in. The current starting up through plate resistor R_1 generates an IR-drop across this resistor, causing the potential of the plate of *T-2* to decrease, relative to the +300 v power supply. This falling potential is transmitted through the coupling condenser, C_2, as a negative-going signal on the grid of *T-1*. This causes the current flowing through *T-1* to decrease, which reduces the IR-drop across R_1 and causes the plate potential of *T-1* to rise (become more positive). This, however, requires the grid of *T-2* to become more positive also, since the latter is connected to the former through the voltage divider resistor R_3.

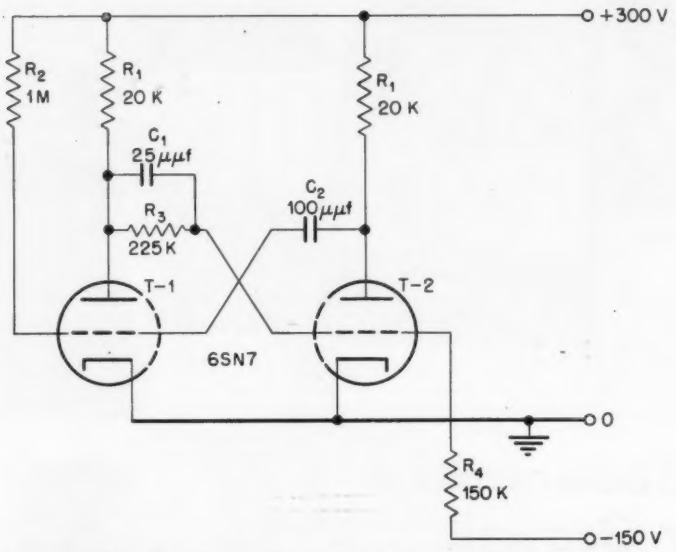

Figure 14. The univibrator circuit, in which a positive pulse applied to the grid of *T-2* turns this tube on and *T-1* off, after which the circuit returns to its starting condition.

Thus, we have seen that the starting up of current in *T-2* causes the current in *T-1* to diminish, which causes the grid of *T-2* to become still more positive, which will cause the current in *T-2* to increase still further. That is, any increase in current in *T-2* causes this current to increase some more, and the new increment in current leads to yet another increment, etc., in the manner of a self-nourishing explosive reaction. This regenerative process continues until tube *T-2* is conducting heavily, and tube *T-1* is cut off. With *T-1* cut off, the regeneration ceases, and the circuit is in a new, temporarily stable state.

However, tube *T-1* is cut off because of the negative charge which has been built up on its grid by transmission from the plate of *T-2* through the capacitor C_2. This charge will leak away through R_2 at

(*Continued on page A310*)

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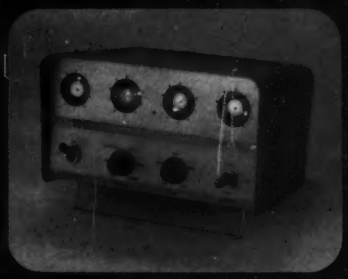

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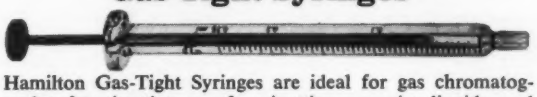

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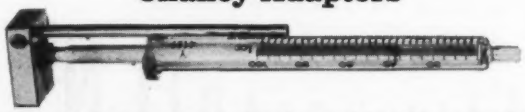

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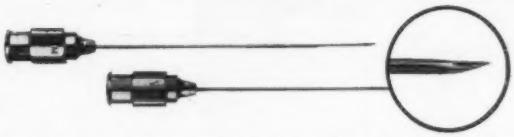

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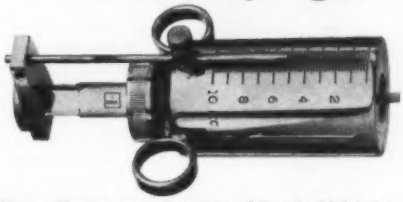

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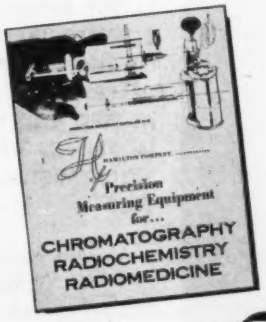

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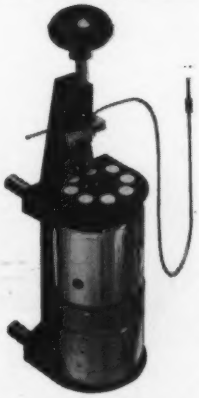

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a rate determined by the time constant $R_2 \times C_2$ (*cf.* Fig. 11). Soon the grid of *T-1* has lost enough of this negative charge that a current can begin to flow in this tube. The starting up of a current in *T-1* causes the potential at its plate to decrease, transmitting a negative-going signal to the grid of *T-2*, etc., and setting in motion a new regenerative effect leading to the shutting off of *T*-2, and the full conduction of *T-1*.

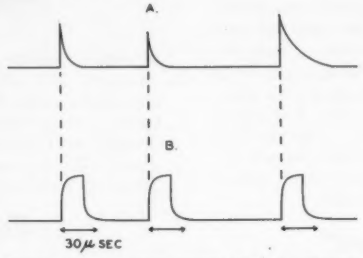


Figure 15. A. Pulses coming from the radiation detector may vary in height and shape. B. After reshaping in a univibrator circuit, the pulses have identical shapes, and a definite duration.

Thus, any pulse of sufficient magnitude fed onto the grid of *T-2* can initiate the flipping over of the univibrator, but the time during which tube *T-1* is cut off, and the delay before the univibrator returns to its starting state are independent of the characteristics of the original pulse. If the output pulse is taken from the plate of *T-1*, Figure 15 shows how the input signal can be reshaped by passage through the univibrator circuit.

Another commonly used pulse-shaping circuit is the *delay line*, a simplified schematic of one type of which is shown in Figure 16. The combination of inductance and capacitance in this network has the effect of retarding the rise of the steepest portions of the pulse relatively more than of the less steep leading and trailing edges, so that a result similar to that shown in Figure 15 is obtained. That is, the top of the pulse may be "clipped" and spread out as a result of passage through the delay line.

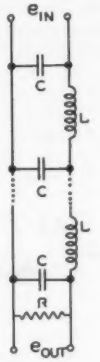
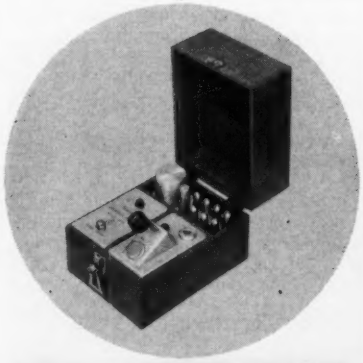


Figure 16. A simple delay line used for the reshaping of pulses.

Non-Overloading Amplifiers

When a pulse amplifier is used for linear amplification of the signals from proportional or scintillation detectors, it is often



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the case that the radiation source generates both small and large pulses, and the presence of the large pulses may prevent the amplifier from faithfully magnifying the small pulses. That is, a large input signal may *overload* an amplifier, by which is meant the fact that the tube currents may be large enough to push the operation of the tube into the non-linear portion of the tube characteristic curve, and to alter the effective plate and grid voltages from their desired range of values. Because of the finite time constants of the various parts of the circuitry, an amplifier does not recover instantaneously from such overloading. However, by careful design of the circuitry, and by careful selection of the amplifier's vacuum tubes, it is possible to minimize these effects. A *non-overloading amplifier* is one which has been so designed. The criterion of the performance of such an amplifier is the time it takes for the output base line to recover its initial value after an overload of several fold over the maximum signal for which the circuit is intended; i.e., several times the signal which gives full-scale deflection of the output stage read-out.

Coincidence Amplifiers

A type of amplifier that is often employed when it is desired to eliminate the interference of high energy radiations from the measurement of a low energy component, or to reduce the background count when measuring a low level source, is the *anti-coincidence amplifier*. The operation of this type of circuit may be most easily understood by considering first the *coincidence circuit*, shown in simplified form in Figure 17. In this case, consider that the circuit components and applied voltages are chosen so that both tubes are normally conducting. If a negative-going signal is placed on the grid of tube *1*, the current through that tube will decrease or be cut off, depending

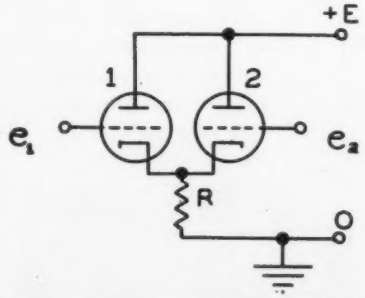

Figure 17. A coincidence circuit, in which the *IR*-drop across the common cathode resistor does not show a large change unless pulses e_1 and e_2 are simultaneous.

upon the magnitude of the signal. This would tend to decrease the current flowing through the common cathode resistor, *R*. However, if the *IR*-drop across the resistor decreases, the cathodes of both tubes become more negative (closer to ground, in the diagram as shown), which

(Continued on page A312)

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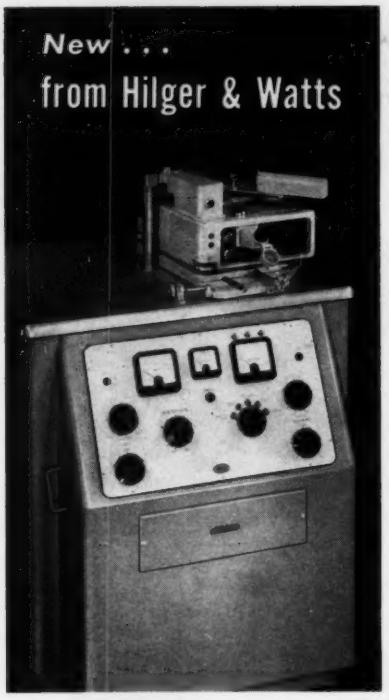

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is equivalent to the grids becoming relatively more positive with respect to their cathodes. If the input signal is large enough to keep tube *1* cut off, this positive-going effect on the grid of tube *1* has no effect, but the positive effect on the grid of tube *2* causes the current through tube *2* to increase. Thus, the decrease in current in tube *1* causes an increase in current in tube *2*, and the net current through the cathode resistor *R* does not change much. However, if the grids of both tubes are fed negative-going signals *simultaneously*, the cathode resistor *R* must show a large decrease in *IR*-drop. Thus, if the output is taken as the voltage drop across this resistor, a large signal is obtained only if both grids are *pulsed in coincidence*. Two radiation detectors are used with this type of amplifier; a high energy nucleon traveling along a line defined by the locations of the two detectors will trigger essentially simultaneous discharges in both, and a coincidence will be recorded by the amplifier. In this way, directional information or selectivity can be achieved.

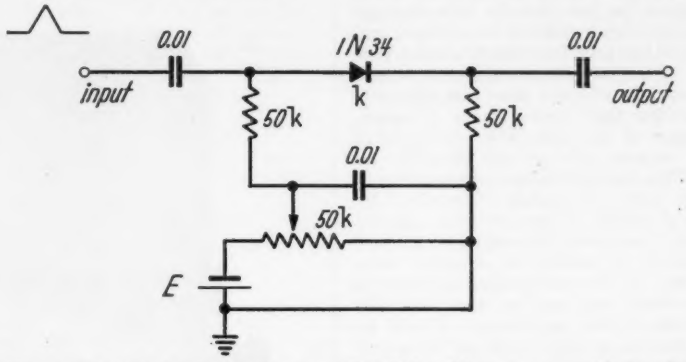

Figure 18. A discriminator circuit based on a rectifier diode. Pulses cause current to flow through the rectifier only if they exceed in voltage the reverse voltage bias applied across the rectifier by the battery and slidewire.

The anti-coincidence circuit is very similar to the coincidence circuit described above, with the exception that one of the tubes is biased so that it is conducting, while the other is biased off. The de-

(*Continued on page A314*)

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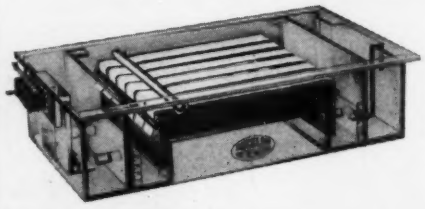

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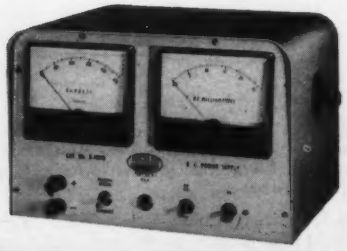

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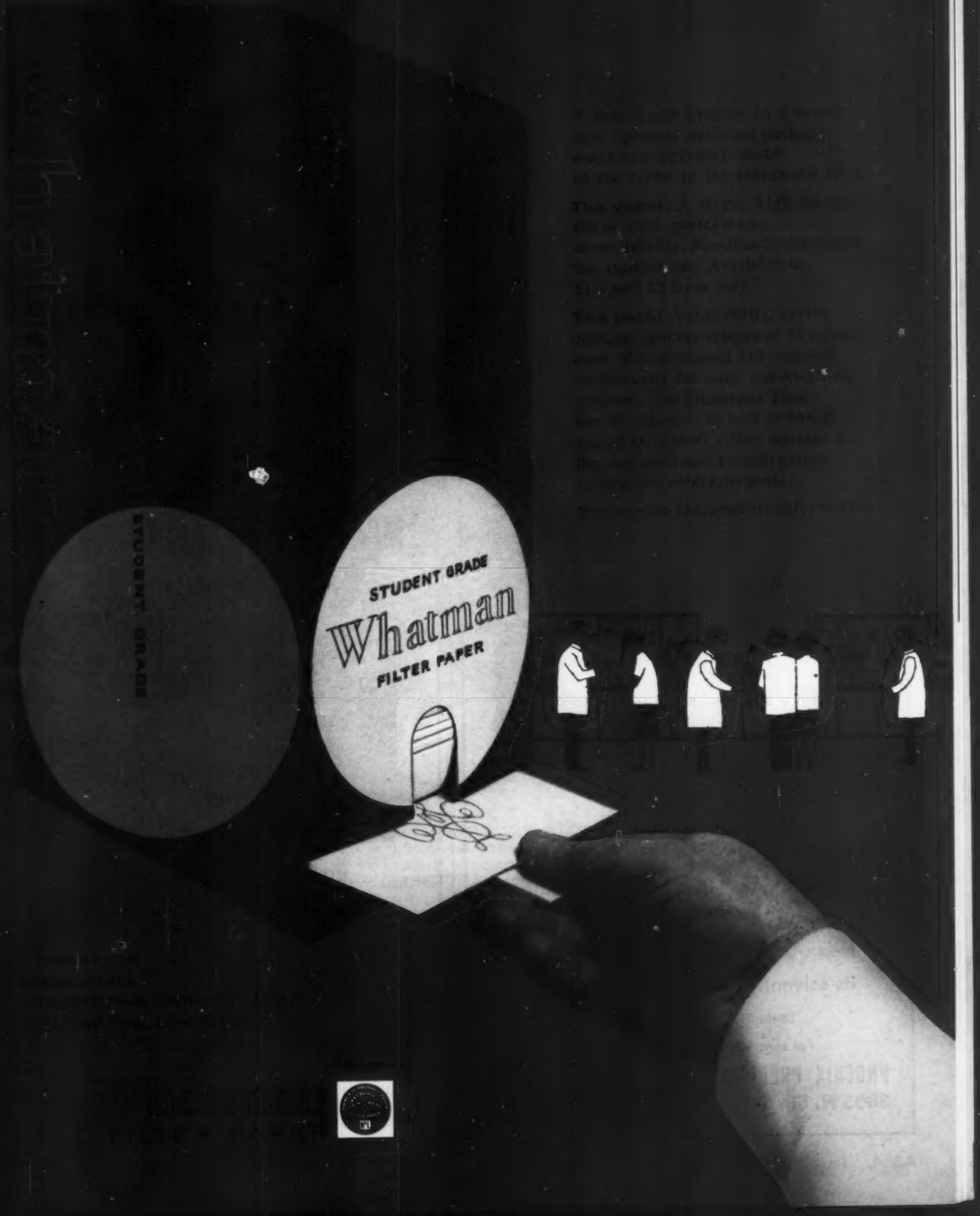

tector that feeds pulses to the tube that is normally on is arranged to feed its grid negative pulses, while the other detector feeds positive pulses to the grid of the tube that is normally off. If either one or the other detector sends a pulse to the circuit, the two tubes will become either both on, or both off, and the cathode resistor current shows a marked change in magnitude. However, if both detectors send in pulses simultaneously, the current in the common cathode resistor is not affected, since under these conditions one tube is on and the other is off (viz., the circuit is in the mirror image of its resting condition).

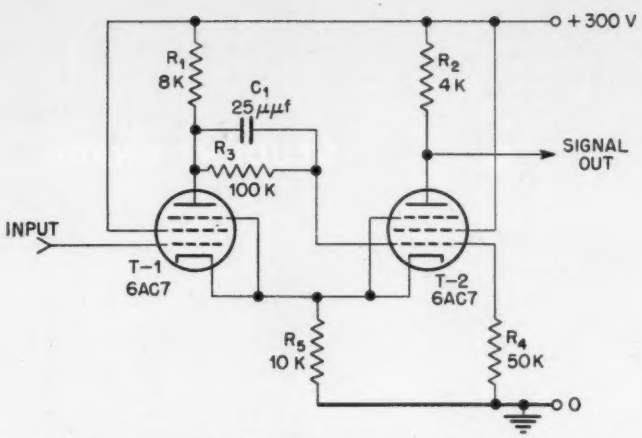

Figure 19. The Schmitt trigger circuit. When the voltage applied to the grid of *T-1* reaches a critical value, the circuit triggers sharply, causing the tube that was conducting to go off, and *vice versa*.

Discrimination

It is often important to amplify only one type of pulse in the presence of another, or to pick out a pulse of given size range from accompanying random noise pulses, and the circuitry employed for this purpose is called a *discriminator*, or *pulse height selector*. One type of circuit used for this purpose is shown in Figure 18. The heart of this circuit is the 1N34 diode, which passes current only when the voltage difference across it is in a certain direction (e.g., positive to the left and negative to the right of the rectifier symbol in the figure). By means of a battery, *E*, and a slidewire, a voltage is applied across the diode in the sense *opposite* to that which produces conduction. If a pulse is fed into this circuit, it will result in a flow of current through the diode only if its voltage exceeds the biassing voltage. Thus, the circuit can be adjusted to pass only those pulses which are bigger than any predetermined size.

Another type of discriminator circuit that is widely used in nuclear detection amplifiers is the *Schmitt trigger*, shown in Figure 19. In this circuit, one of the tubes is normally conducting and the other one is cut off. When the voltage applied to the grid of the cut-off tube is made more positive, a critical value is reached at which a regenerative effect sets in (see discussion above of univibrator circuit) that turns this tube on, and turns the other tube off. This triggering effect can be set to occur for any desired voltage level, so this circuit can be employed to announce when a signal has reached a given value, and, in fact, can tell whether the signal has approached that value from above or from below.

The action of the Schmitt trigger can be understood qualitatively as follows. Consider that tube *T-1* in Figure 19 is not conducting because its grid is negative with respect to its cathode. If this grid

(*Continued on page A316*)

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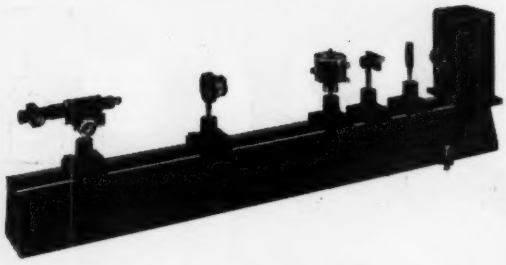

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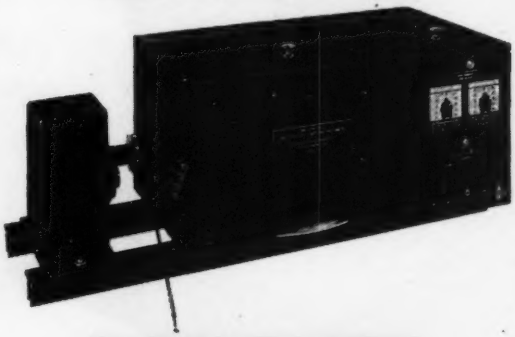

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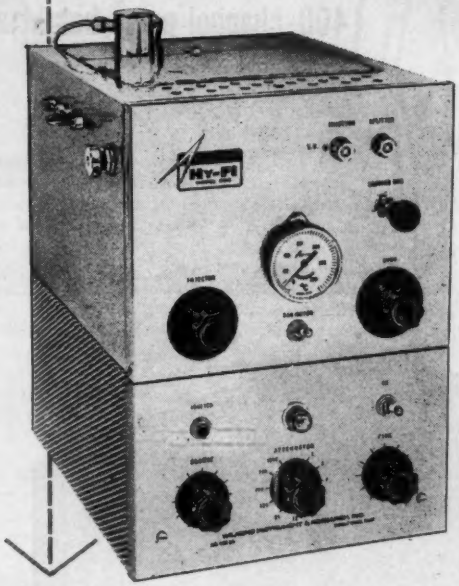

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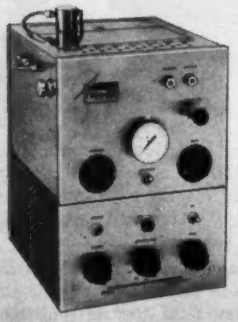

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is gradually made more positive, nothing happens until the grid potential has risen sufficiently close to the cathode potential to permit some tube current to flow. When this current starts in *T-1*, regeneration sets in, for the current causes the potential of the plate of *T-1* to decrease, which makes the grid potential of *T-2* more negative, and causes the current in *T-2* to decrease. The net effect of the increase in current in *T-1* and the decrease in *T-2* is a small decrease in the total current through the common cathode resistor, R_k. This makes the cathodes more negative than they were, and is equivalent to the grid of *T-1* becoming more positive. This further increases the current in *T-1*, further reduces this tube's plate potential, causes the grid of *T-2* to become still more negative, etc., and the regeneration rapidly leads to the cutting off of *T-2*, and the full conduction of *T-1*. After this triggering has occurred, making the grid of *T-1* more positive by means of the input signal merely causes this tube to conduct more heavily, but does not change the state of the circuit. If the input signal is reduced in magnitude, the regeneration sets in in reverse when the critical level of potential is reached.

A *single channel differential analyzer* contains two discriminator circuits, so arranged that one of the discriminators acts as a lower gate or window to pass all pulses *larger* than a preset value, and the other discriminator acts as an upper gate to pass only those pulses having *smaller* amplitudes than its preset value. Thus, the two discriminators provide a selected pulse height interval, and only pulses whose heights lie within this interval are accepted for amplification. By varying the locations of the upper and lower windows, the entire distribution of pulse heights produced by a radiation source can be determined. This is the basis of the relatively new and rapidly developing field of *pulse height spectrometry*. A variety of pulse height analyzers employing single channel and multi-channel selectors is now commercially available.

Cathode Follower

In the coupling of an amplifier to a radiation detector on one side, and to a read-out device on the other, it is often essential to have an *impedance matching* stage between these units. If the input impedance of a device is low, the device will draw appreciable current from any source to which it is connected. If the output impedance of a source is high, it may be incapable of delivering appreciable currents. A circuit that can be used as a coupling stage to permit the output of a high impedance source to control a low impedance circuit is the cathode follower, shown in schematic diagram in Figure 20. The signal from the high impedance source is applied to the grid of the vacuum tube through the high impedance capacitor-grid resistor circuit, and negligible current is drawn from the source. The signal modulates the tube current, and the changes in the

latter can be observed as variations in the *IR*-drop across the cathode resistor, R_K. Since the tube current is relatively large, and R_K is a small to moderate resistance, the *IR*-drop across R_K can be used to drive low input impedance devices. The circuit derives its name from the fact

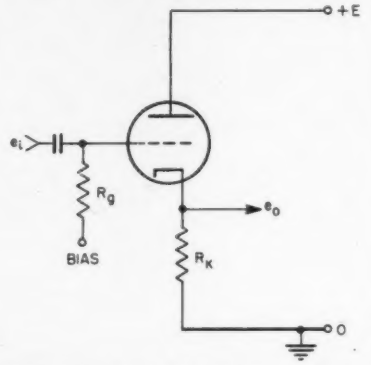

Figure 20. The cathode follower circuit for impedance matching. The input to this circuit is fed in through a high impedance; the output is taken across the low impedance, R_K.

that the variations in the *IR*-drop across the cathode resistor precisely follow the variations in the input signal.

Scalers

The output from a radiation detector-pulse amplifier combination consists of pulses that are randomly spaced in time, and occur with a frequency determined by the strength of the radioactive source. In order to count the individual pulses, and register their number, it is necessary to devise a high-speed counting instrument capable of responding to impulses that are only microseconds apart. The function of a *scaler* is to provide an electronic means of scaling down the frequency of pulsing of the output of the amplifier without losing any information, so that the scaled-down rate of pulsing can be presented in a form suitable for read-out.

One of the most widely used of scaling circuits is the *scale-of-two, binary,* or *flip-flop* circuit, shown in Figure 21. This circuit has two stable states, viz., the two mirror images in which one of the pair of tubes is conducting, and the other is cut off. Since the plate of each tube is connected through an impedance to the grid of the other tube, the current that flows in the tube that is conducting produces an *IR*-drop in its plate circuit that drives the grid of the other tube negative enough to cut it off. The trick in the scale-of-two circuit is to introduce the pulses coming from the amplifier in such a way as to cause the circuit to flip over from one of its states to the other one. The detailed operation of this circuit can be understood by reference to Figure 21.

Assume that tube *T-3* is conducting, and *T-4* is cut off. The twin diode, *T-1* and *T-2*, has its two plates connected to the plates of the two scaling tubes,

(*Continued on page A319*)

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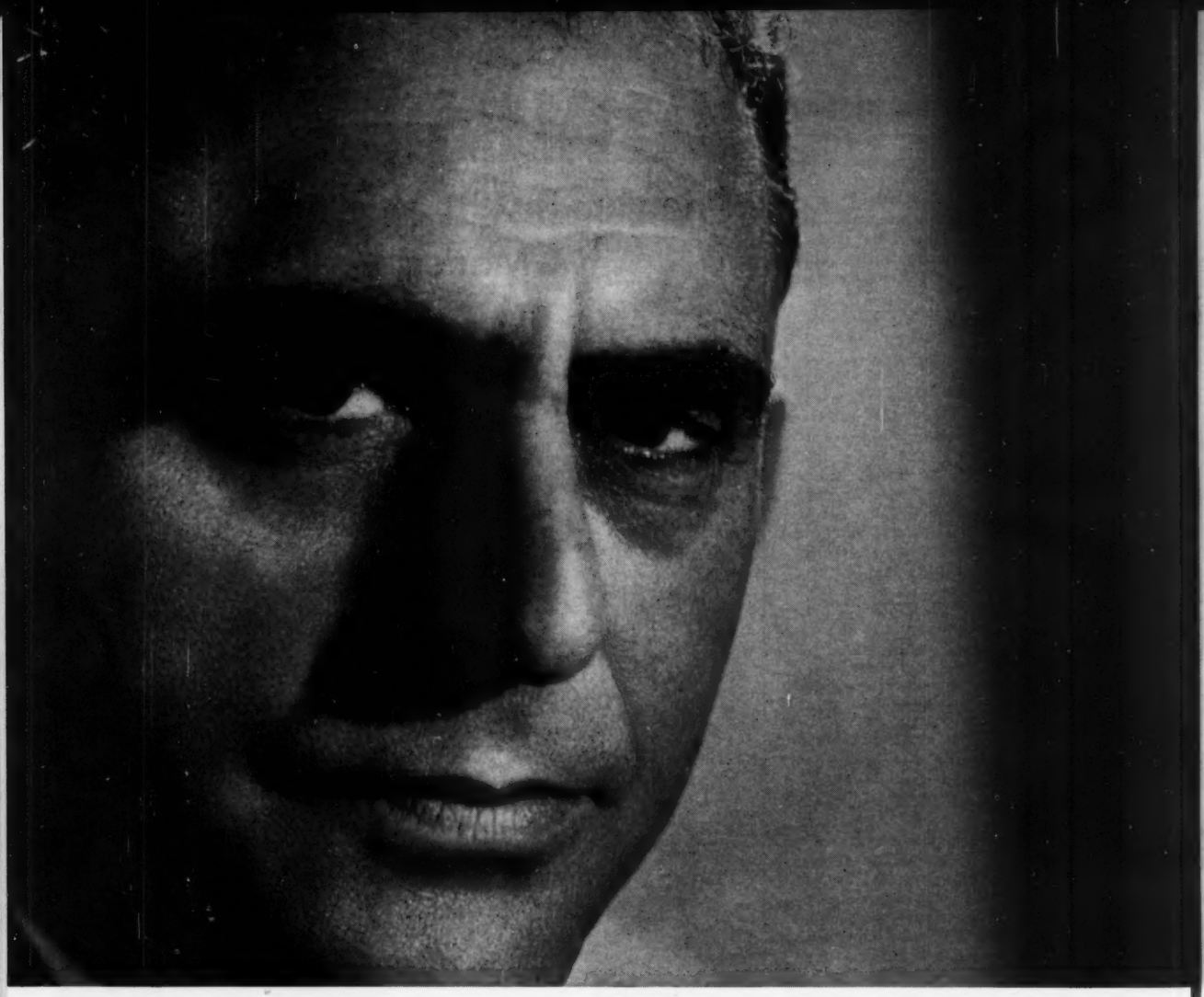

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T-3 and *T-4*. The cathodes of the twin diode are normally at a potential equal to that of the plates, and no current flows through *T-1* and *T-2*. The pulses to be scaled down are applied to the twin diode cathodes, driving them negative with respect to their plates, and permitting current to pass through both

(*Continued on page A322*)

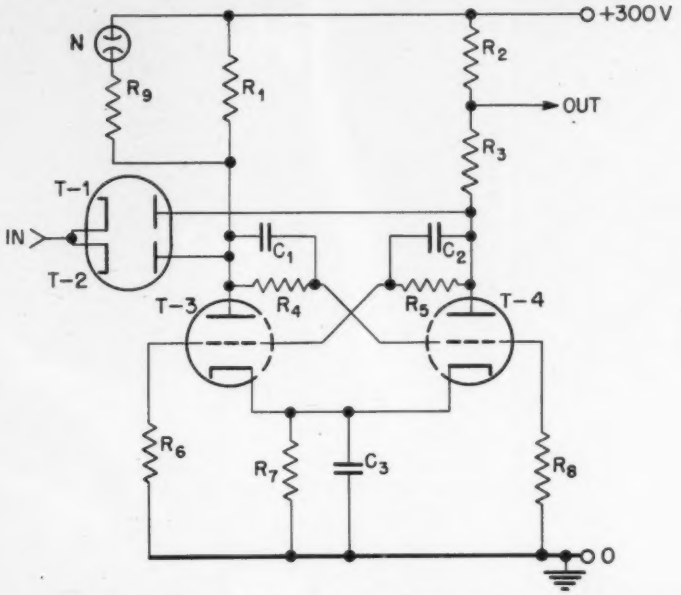

Figure 21. The scale-of-two circuit, for yielding an output having exactly one-half the frequency of the input. *T-1* and *T-2* are rectifier tubes through which the input pulses are fed to the two trigger tubes, *T-3* and *T-4*.

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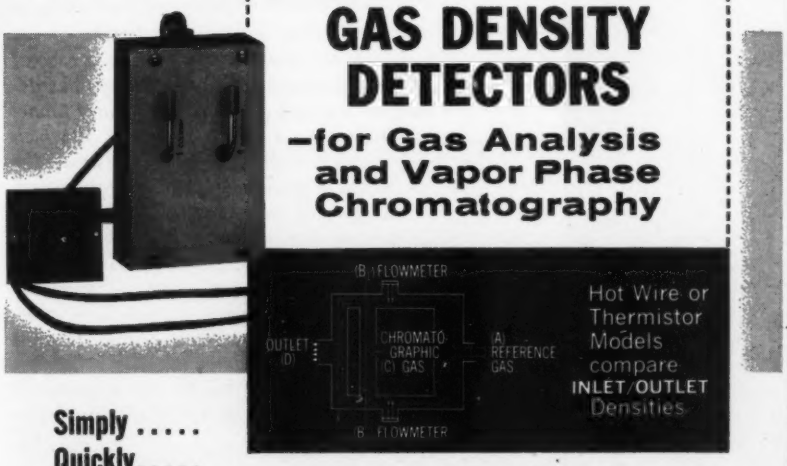

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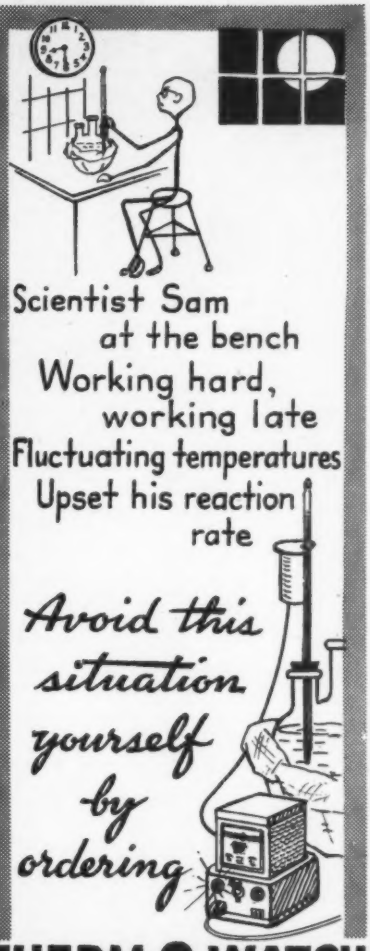

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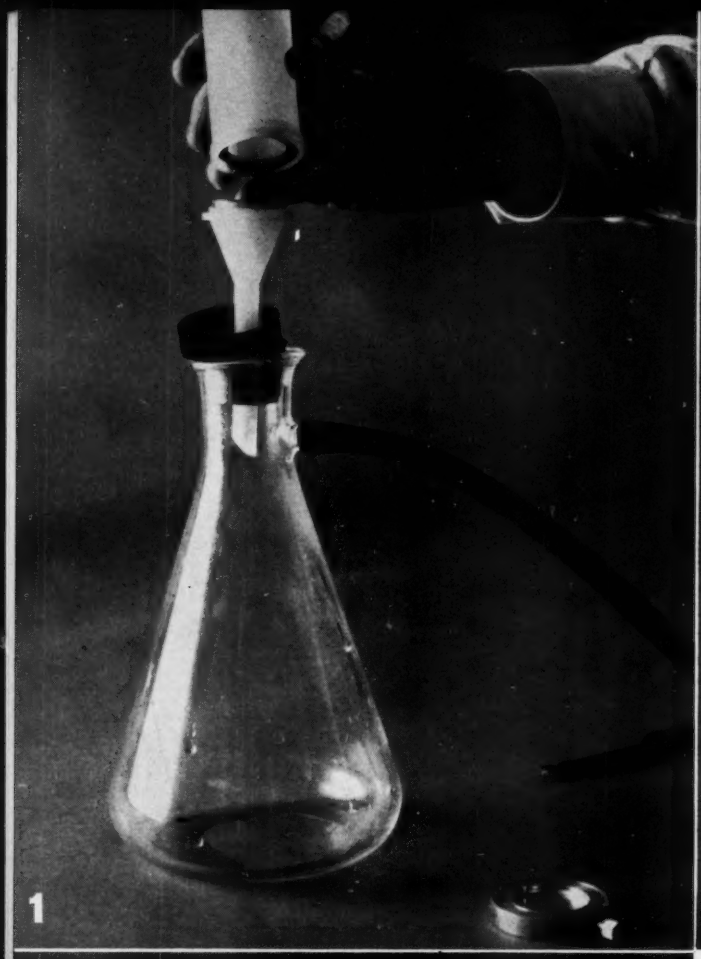

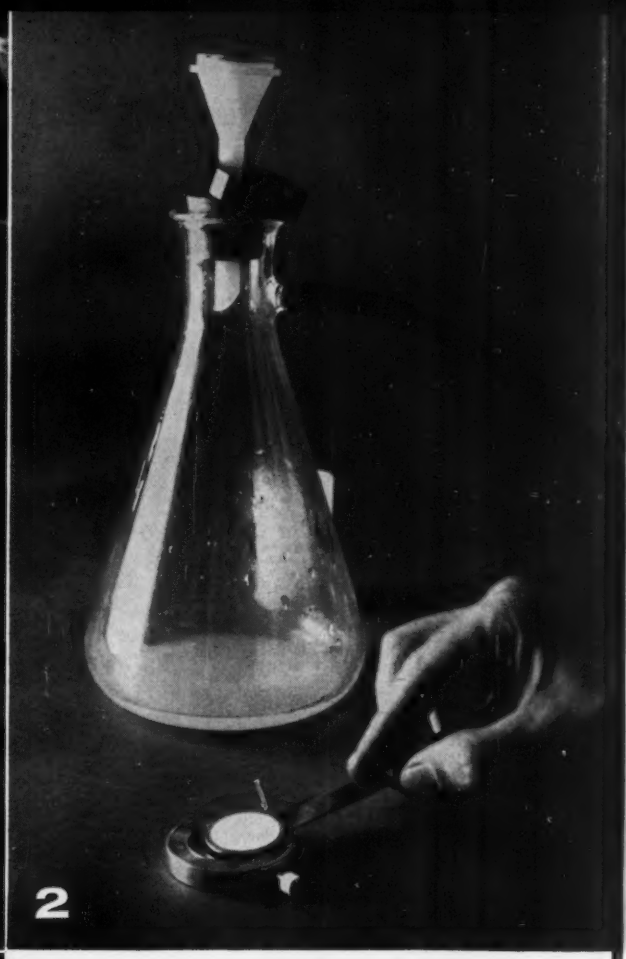

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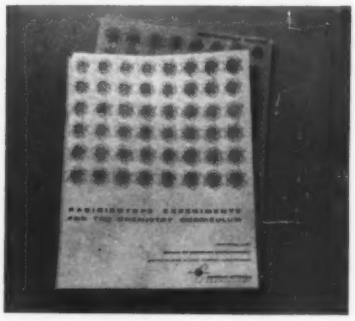

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tubes. These currents flow through the plate resistors R_1 and R_3 of both scaling tubes, causing the plates of *T-3* and *T-4* to become more negative in potential than they were. Since these plates are coupled to the grids of the other member of the pair, the effect of the original pulse is to produce negative-going potentials on the grids of both scaling tubes. Since the grid of *T-4* is already cutting this tube off, an additional negative-going pulse on this grid has no effect. However, *T*-3 was conducting, and a negative-going pulse on this grid causes the tube current to begin to decrease. This raises the potential at the plate of *T-3*, which in turn raises the potential of the grid of *T-4*, which causes current to start up in *T-4*, lowering the potential of the plate of *T-4*, which causes the grid of *T-3* to become more negative, decreasing still further the current in *T-3*, etc., etc. The regenerative process rapidly leads to the cutting off of *T*-3 and the full conduction of *T-4*. Thus, the introduction of a pulse has flipped the circuit over from (*T-3 on, T-4, off*) to (*T-3 off, T-4 on*).

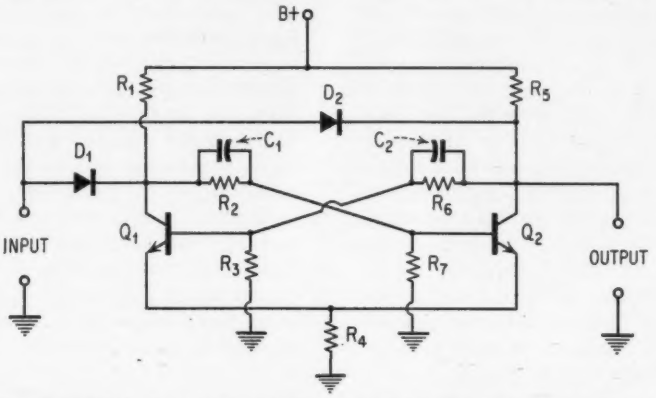
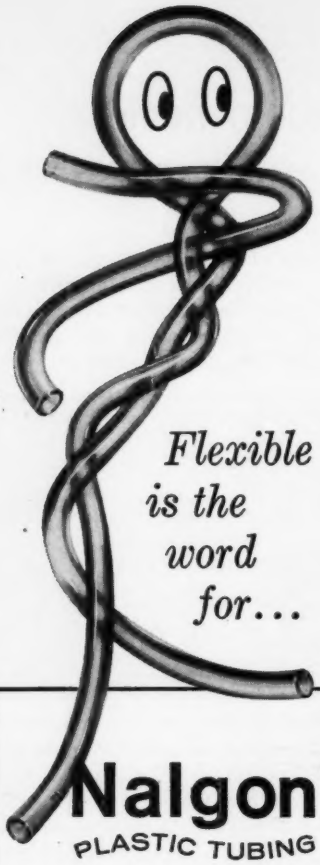


Figure 22. A transistorized scale-of-two circuit. *D-1* and *D-2* correspond to the rectifier tubes in Figure 21; *Q-1* and *Q-2* correspond to the trigger tubes.

The neon bulb, *N*, is in parallel with

(*Continued on page A324*)



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the plate resistor, R_1, of *T-3*. When *T-3* is conducting, the *IR*-drop through R_1 corresponds to a sufficient voltage to light the bulb. When *T-3* goes off, the light is extinguished. Hence, the light goes on for every other pulse fed to the circuit; e.g., if four pulses have been fed in, the bulb has been lit twice, and extinguished twice. That is, the frequency of lighting of the bulb is exactly one-half of the frequency of the pulses; if the bulb (or, equivalently, the *IR*-drop across one of the plate resistors) is taken as the output signal, the frequency of the input has been scaled down by a factor of two.

The output from this scale-of-two circuit can now serve as the input to a second scale-of-two circuit; i.e., the circuits can be *cascaded*. If two binary circuits are cascaded, the output at the last stage has been scaled down by a factor of 4; if three, by 8; if n, by 2^n.

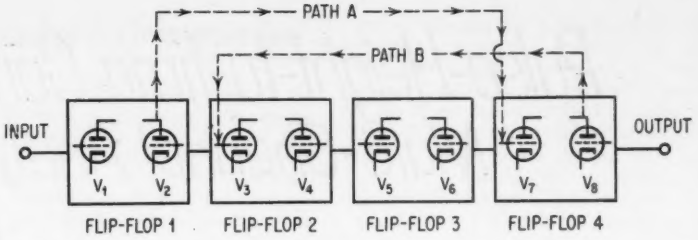

Figure 23. Schematic representation of the principle that permits four scale-of-two stages to be cascaded and modified with feedback loops to yield a scale-of-ten counting arrangement.

Binary scalers are currently available with final-stage scaling factors of 1024, and higher.

Figure 22 shows a scale-of-two circuit based upon the principles outlined above, but in which NPN-type transistors are employed in place of vacuum tubes. In this circuit, the collector corresponds to the plate of the triode, the emitter to the cathode, and the base to the grid.

The binary system of recording counts is simple electronically, but creates some arithmetic difficulty in making computations according to our decimal (i.e., scale-of-ten) system. Therefore, considerable ingenuity has gone into the design of circuits that permit the fundamental scale-of-two to be cascaded in such a way as to yield a scale-of-ten counter. The principle of this method of achieving a decimal scaler is shown schematically in Figure 23. This consists of 4 scale-of-two circuits, such as would be found in a scale-of-sixteen scaler. However, when the tenth pulse is fed in, V_2 comes on and a signal is sent over path A to cut off V_7 and turn V_8 on. Although V_2 was also turned on at the second, fourth, sixth, and eighth pulses, V_7 was off at those times, and the signal in path A had no effect. When V_2 comes on, it normally turns V_3 on, but on this tenth pulse, the turning on of V_8 sends a pulse back over path B that prevents V_3 from being affected by V_2. In this way, there result ten different combinations of the four bistable flip-flop states produced successively by ten pulses. Each combination can be assigned a digit, and a scale-of-ten *decade unit* is the result. An example of such a decade scaler circuit is given in Figure 24.

A scaling decade can be achieved in a much simpler fashion by the use of a *beam switching*, or *glow transfer* tube. This is a tube containing a filling of neon or other noble gas, a permanent magnet surrounding the tube, and three sets of ten each of electrode elements plus a single cathode. The electrodes consist of a grid, a plate, and a spade, respectively, and ten groups of these three electrodes are spaced around the central cathode as shown in the Figure.

Consider that a discharge exists in the tube so that an electron beam flows from the central cathode to one of the plates (No. 0 in the figure). When a pulse is applied to this tube, it is arranged to make the ten grid electrodes (all of which are connected to a common point) become more positive. The glow discharge will then move over toward that grid and then

(*Continued on page A327*)

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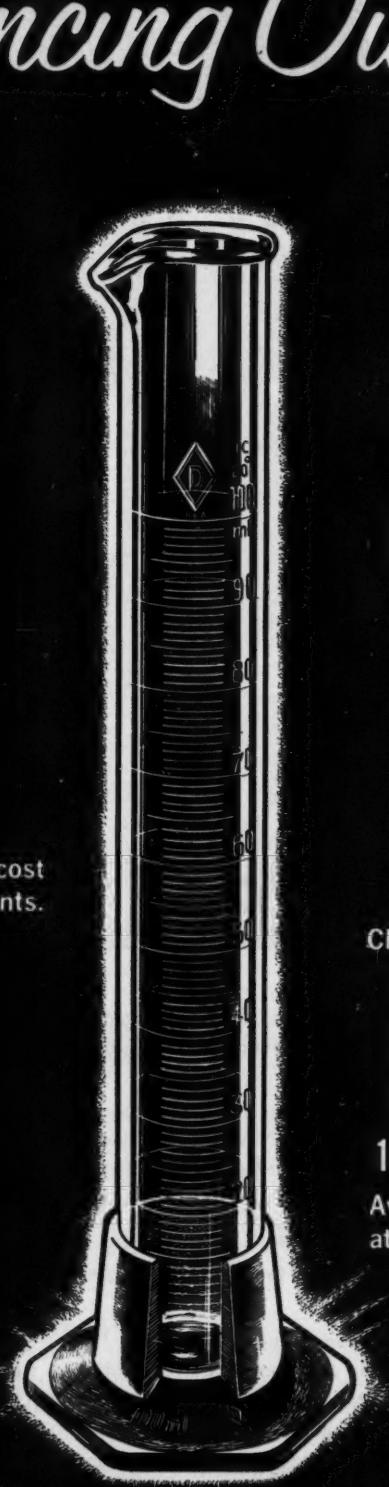

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climb along the beam-forming spade electrode as the pulse dies away. The discharge "locks in" on the plate (No. 1, in the figure) toward which the shape of the spade has directed it. The glow will then remain here until the adjacent grid is made positive, by virtue of a new pulse coming in, as a consequence of which the glow will move over to plate No. 2. Each pulse, applied simultaneously to all grids, advances the glow by only one position at a time, and always in the same direction (clockwise, in the figure). Thus, the location of the glow discharge at any instant shows how many pulses have been fed into the scaling unit, in units of ten. These beam switching tubes can also be cascaded, so that the second stage tube gets its pulses from the No. 10 (i.e., 0) position in the first stage tube.

Rate Meters

The actual counting of total numbers of discrete pulses over precisely defined time intervals can be avoided through the use of a circuit which totalizes the pulses in a differential way, so that the condition of the circuit is sensitive to the rate of pulsing. This is called *counting-rate*

(*Continued on page A328*)

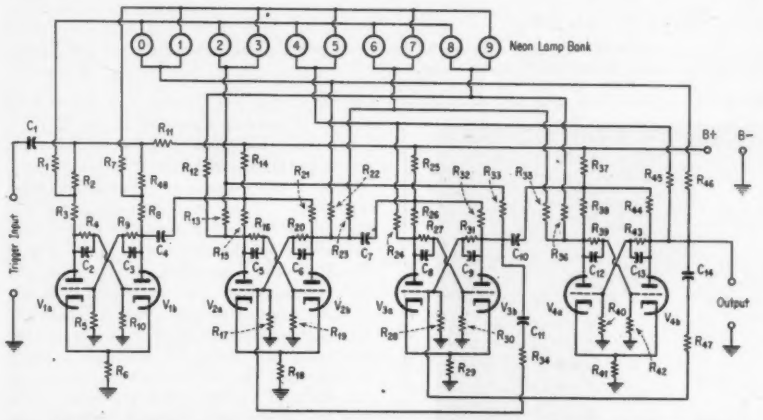

Figure 24. Circuit diagram of a decimal scaler based on the principle illustrated in Figure 23.

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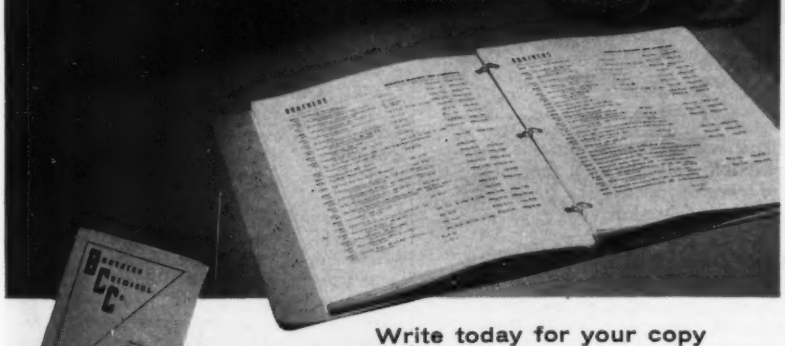

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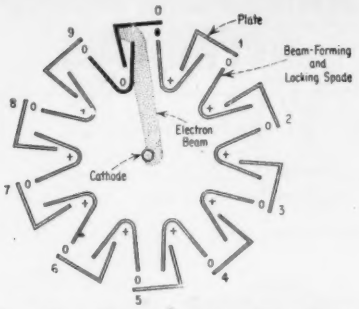

Figure 25. Schematic diagram of the electrode configuration in a beam switching tube. The grid electrodes are the small circles located between each plate and spade. A glow discharge occurs between the central cathode, and one of the plate electrodes.

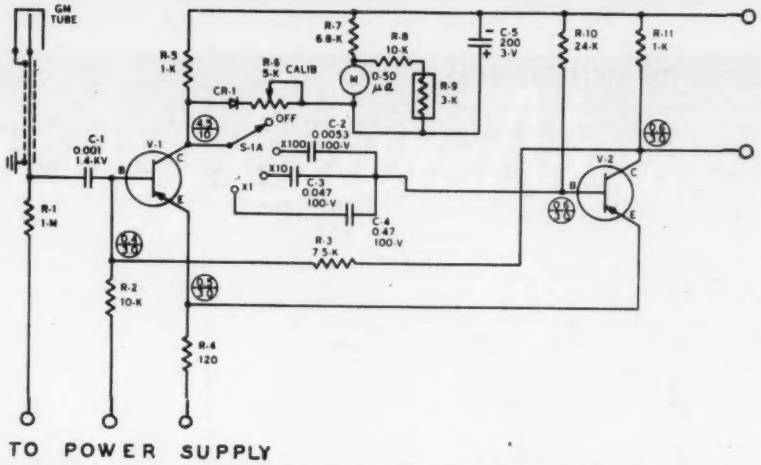

Figure 26. A portion of the circuit diagram of the counting-rate meter employed in the Anton Electronic Labs' Model 6 Radiological Survey Meter.

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circuitry, and involves two principal features. Provision must be made, if it is not already included in the amplifier that precedes this circuitry, to shape the pulses so that every pulse is equal in height and duration. This is commonly accomplished by the use of a univibrator circuit (see above for detailed explanation of this circuit). The counting-rate circuit is then arranged so that each pulse puts a definite amount of charge on a capacitor. Simultaneously, some of the charge on the capacitor leaks off through a high resistance. The steady state charge on (or, voltage across) the capacitor is thus due to the dynamic balance between the rate at which pulses are fed in, and the rate of leakage of the stored charge. A voltmeter connected across the capacitor can be calibrated to read directly in counts per minute.

An example of a count-rate meter used in a commercial survey instrument (Anton Electronic Labs Model 6 Radiological Survey Meter, $139.50) is given in Figure 25. The two transistors, *V-1* and *V-2*, constitute a univibrator; pulses from the G-M tube cause *V-2* to go off and *V-1* to come on. *V-1* stays on for a time determined by the product of *R-10* times the capacitance chosen by the selector switch. This results in a voltage pulse at the collector of *V-1;* this pulse passes current through the silicon rectifier, *CR-1*, and adds charge to the capacitor, *C-5*. The meter, *M*, is in parallel with the storage condenser, so that some of the charge leaks off through it. The deflection of the meter is therefore proportional to the rate of pulsing of the G-M tube.

A counting rate meter is very useful if changing levels of radioactivity are to be determined, as in the surveying of an area, or the monitoring of a flowing stream. The counting rate circuit adapts very simply to the driving of a continuous recorder, so that a continuous and permanent record of the radiation level is obtained. However, in relating the output of a counting rate meter to radioactivity level, it is important to take into account the errors that may result from the relatively large time constant necessary in the tank circuit (storage capacitor plus its shunting resistance).

(*Continued on page A330*)

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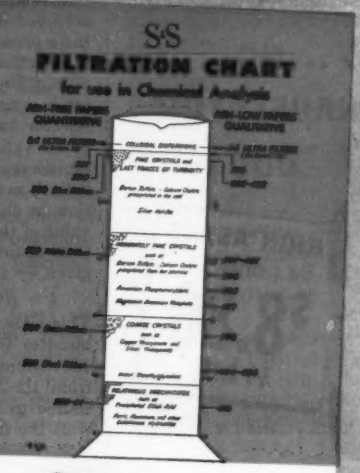

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Chemical Instrumentation

Since the storage condenser is simultaneously charging and discharging, the time required for its equilibrium state to be achieved depends upon the rates of both these processes. The former depends upon the radioactivity level (N counts per minute) being measured, whereas the latter is constant for a given setting of the selector switches of the instrument (viz., given values of R and C). Hence, the *equilibrium time* of a counting rate meter, defined as the time necessary for the deflection to change from zero to the average value of the counting rate, is a function of that counting rate, in a manner that is given by the following equation.

$$t = RC(1.15 \log_{10} 2NRC + 0.394)$$

This time can be of the order of several minutes for counting rates of less than 1000 counts per minute. When switching from the measurement of one radiation source to another, it is not necessary to wait the full time specified by this equation, since the storage condenser is not starting from a state of zero charge. Indeed, the smaller the change is in intensity level, the shorter may be the waiting period before reading the meter.

The probable error of an instantaneous reading of a counting rate meter is a function of the counting rate and of the time constant of the tank circuit, as shown by the equation:

$$\text{P.E.} = \frac{0.6745}{\sqrt{2NRC}}.$$

This error can be reduced by averaging the reading over a period of time.

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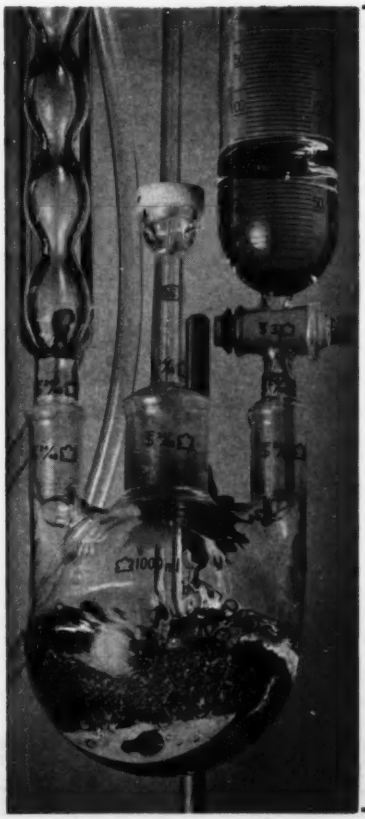
Next: Conclusion of the survey of nuclear radiation electronic gear.



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Edited by William G. Kessel

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New Apparatus and Equipment

▶ Wilkens Instrument and Research Inc., P. O. Box 313, Walnut Creek, California, who specialize in gas chromatography and manufacture the Aerograph Gas Chromatograph line, announces the new Aerograph Hy-FI (hydrogen flame ionization detector.) The Hy-FI is a complete, high temperature programming, Gas Chromatograph with Hydrogen Flame Ionization Detector. The phenomenal sensitivity and high operating temperature extends analytical possibilities into a whole new area not possible using thermal conductivity instruments. The Aerograph Hy-FI is especially useful for the analysis of sex hormones, flavor extracts, air and water pollution, etc.

▶ A new automatic laboratory titrator has just been introduced by Coleman Instruments, Inc., 45 Madison St., Maywood, Illinois, manufacturer of instruments for chemical analysis. Named the Coleman Titr*ion*, this titrator quickly, precisely and automatically performs any titration in which the end point can be related to a reproducible electrode potential, including pH, redox and conductometric procedures.

▶ An effective solution to the nuisance of mill noise in busy laboratories, or in process plants operating large number of mills, is found in the new line of sound-insulated Jar Mills now being offered by the U. S. Stoneware Co., Akron 9, Ohio.

▶ A new Vacuum Plastic Glove Box has been introduced by the Manostat Corporation 26 N. Moore St., New York 13, N. Y. Designed in a cylindrical shape, with welded construction and dome coverplates, this latest Vacuum Glove Box can withstand full vacuum and permits the user to introduce any controlled atmosphere with ease and safety.

▶ A series of freezers, Cryostro, that can provide for temperature ranges as low as −200°F, are now available from Instrumentation Associates, Inc., 17 W. 60th St., New York 23, N. Y.

▶ The J. T. Baker Chemical Co., Phillipsburg, New Jersey, has developed a new "Shure-Grip" 5-pint bottle for reagent acids, incorporating a finger-fitted jug-type handle to provide a safe, sure grip when lifting, pouring or carrying.

▶ Seven new chemical analytical instruments were introduced by the Instrument Division of the Perkin-Elmer Corp., Norwalk, Connecticut, at the recent Pittsburgh Conference. Among the products is a high performance atomic absorption spectrometer as well as other new instruments which cover the techniques of infrared spectroscopy, ultraviolet and visible spectroscopy and gas chromatography.

▶ The Dyna-Slide Co., 600 S. Michigan Ave., Chicago 5, Illinois, a leading designer and manufacturer of special slide rules, has placed on the market a Do-It-Yourself Special-Purpose Slide Rule Kit. With this kit an individual can design and construct his own special-purpose slide rule for doing recurring calculations connected with his work. An illustrated booklet of instructions shows how to assemble different types of slide rule blanks from the parts included in the kit. The 25-page booklet also explains the theory of slide rule design and gives stepwise procedures on how to express

(*Continued on page A335*)

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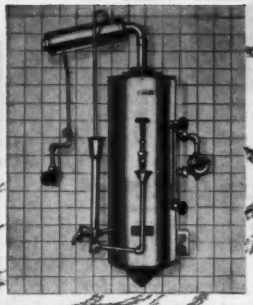

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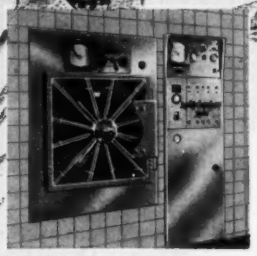

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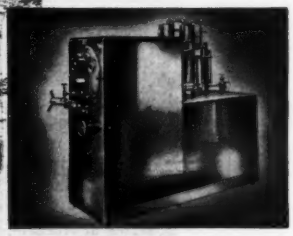

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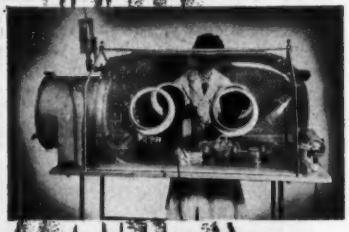

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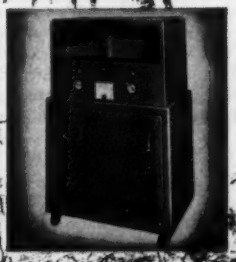

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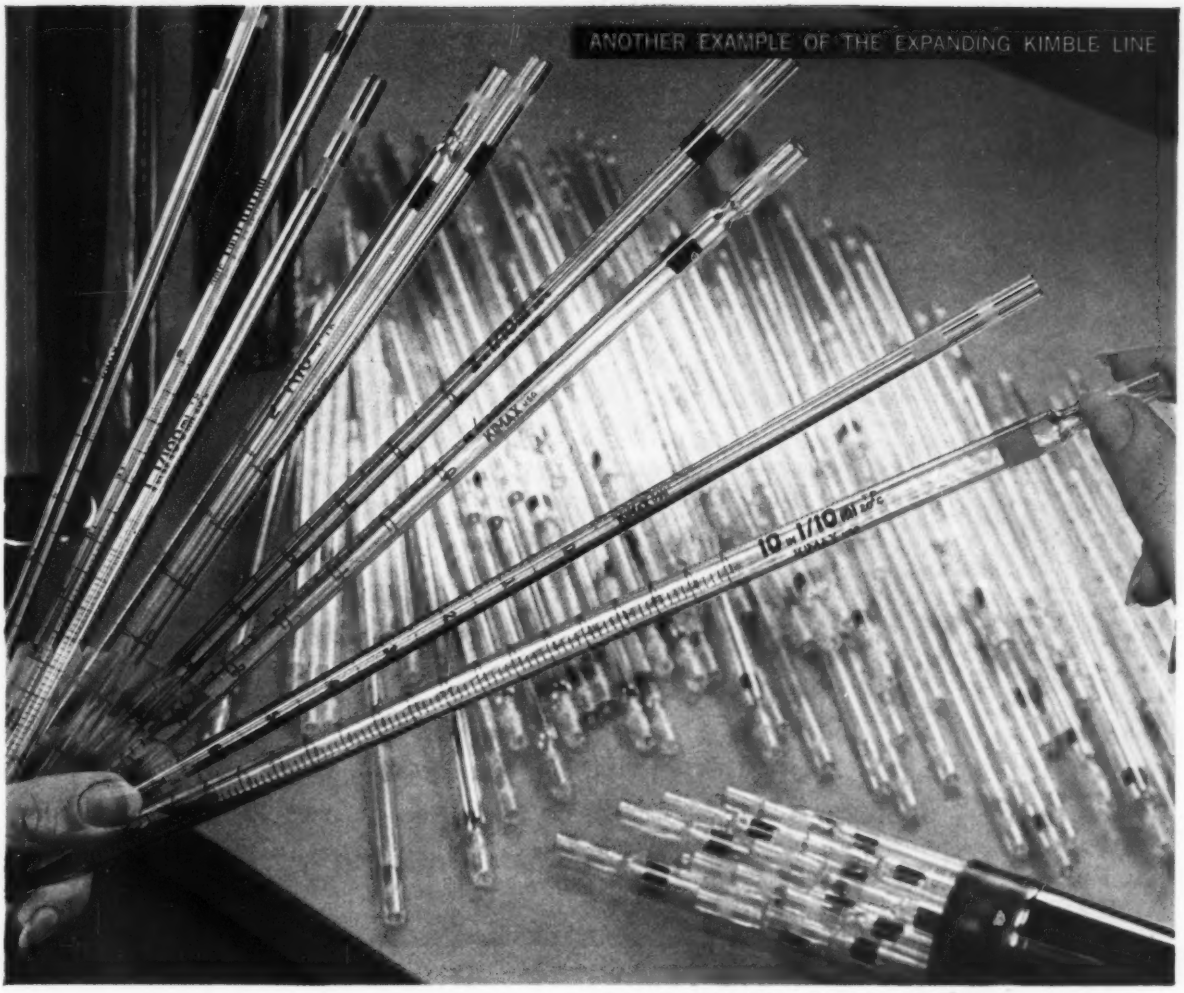

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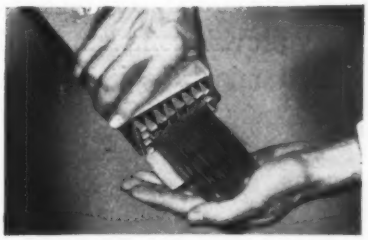

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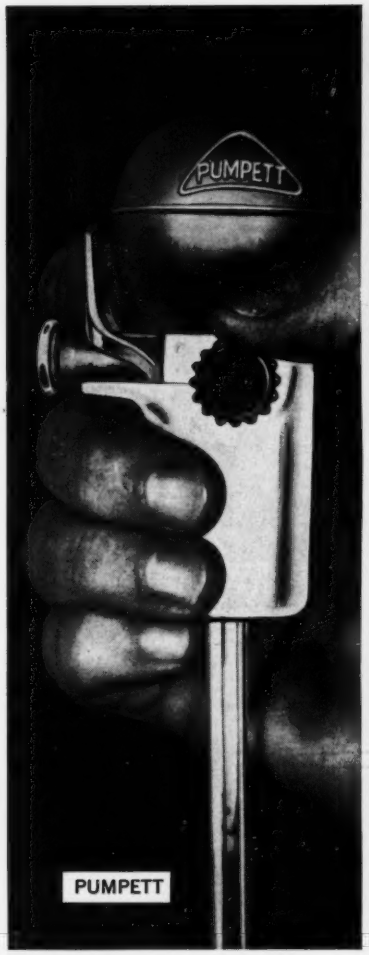

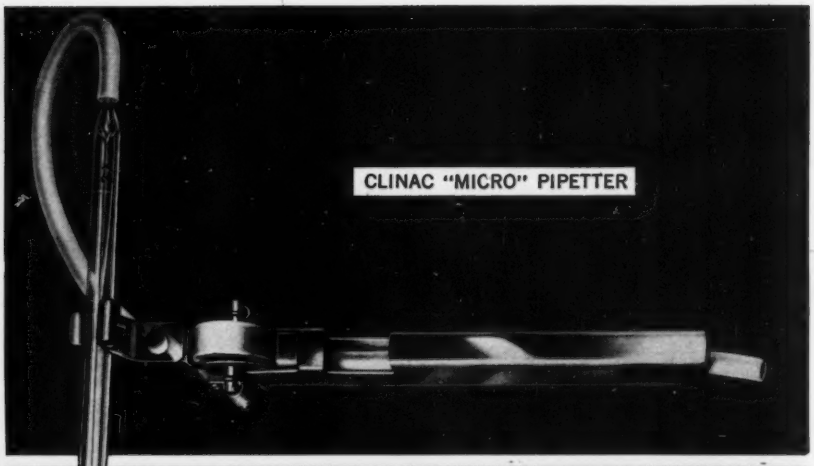

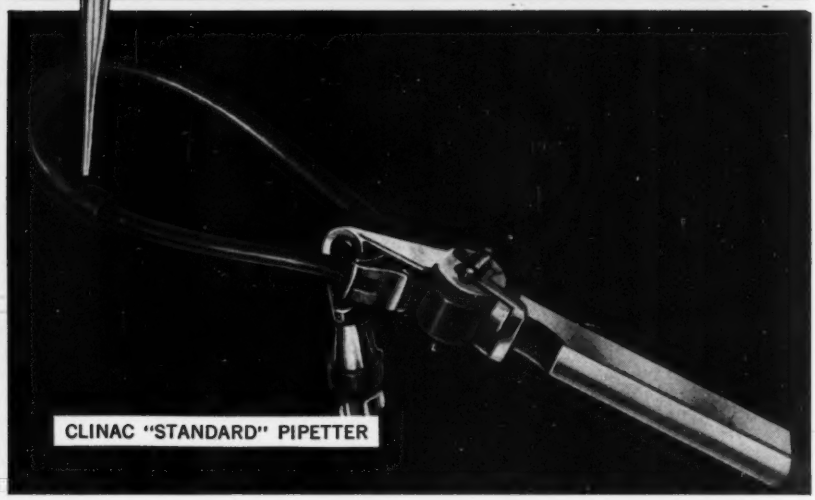

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▶ Production of a compact, high pressure solenoid valve for use in fluid (liquid and gas) control in laboratories has been announced by General Magnetics, Inc., 2014-A Foshay Tower, Minneapolis 2, Minnesota.

▶ Two styles of test tube heaters manufactured by Research Specialities Co., 200 So. Garrard Blvd, Richmond, California, for laboratory use are described in the January issue of the *RSCo Review*. Both types hold temperatures within ±1°C. up to 300°. They are designed for continuous operation and are known to have been used at 250° and higher for 800-hour tests.

▶ Comroe Laboratories, 5208 So. Lake Park Ave., Chicago 15, Illinois, announce the availability of the "Autotherm" self-powered, portable, direct reading conductivity meter for monitoring the solids content of liquids. "Autotherm" automatically compensates for liquid temperatures from 32° to 212°F.

▶The J. T. Baker Chemical Co., Phillipsburg, N. J. announces the development of a new screw cap container for various ethers which enables chemists to open and close the ether container easily and conveniently. The new screw cap container features a special cap liner made of a unique combination of resilient sealing materials. A slight finger pressure will tighten the cap sufficiently to assure a leak-proof seal. The container pours evenly from a large opening and is safe and easy to open. No sharp edged tool is needed.

▶A new, low-cost, nuclear organic-moderated activation demonstrator, which allows students to perform neutron radiation experiments with complete safety, is now available from Atomic Accessories, Inc., 811 W. Merrick Rd., Valley Stream, N.Y. Model ND-217, "Nomad I" uses low-level neutron sources to study basic neutron behavior and to produce tracer quantities of short-lived radioisotopes. It consists essentially of a mobile aluminum drum, filled with high-purity paraffin that acts as a neutron moderator and as shielding. Vertical ports are used as experimental facilities and are located at discrete diffusion lengths from a central "source" port. "Nomad I" is also an ideal storage place for plutonium-beryllium neutron sources such as are available on loan from the A.E.C. *Bulletin 217* describes this equipment and is available on request.

▶A new high speed decade scaler with preset count for use with automatic sample changers is offered by Nuclear Measurements Corp., 2460 N. Arlington Ave., Indianapolis 18, Indiana. Called Model DS-1AP, the instrument is designed for precision counting in the clinical,

(*Continued on page A336*)

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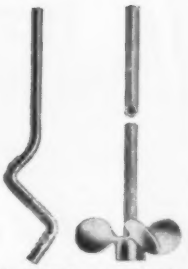

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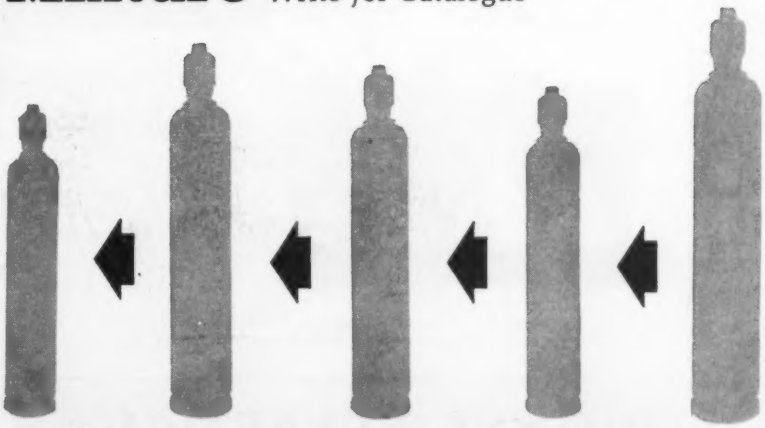

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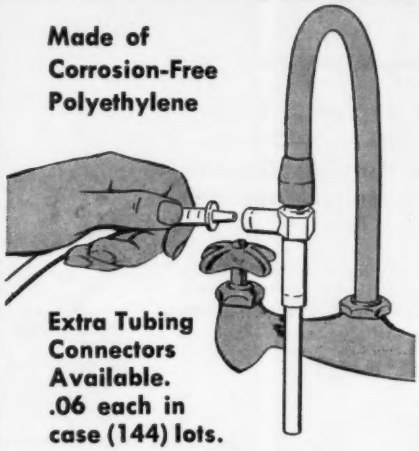

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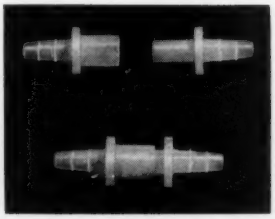
Operates on water pressure from 11 lbs. up. All-polyethylene. Integral check valve not affected by fumes or corrosive filtrate. Take up to 3/8" tubing—connects and disconnects instantly. Has 3/8" IP male thread faucet connection.

Priced at $1.30 Each in case (72) lots.



Priced .25 ea. in case (72) lots.

QD CONNECTORS

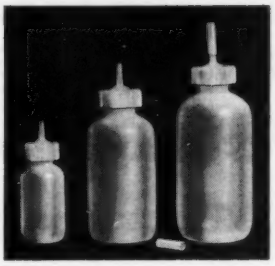
A quick disconnect flexible tubing connector. Designed particularly for vacuum applications. Also useful for connecting water lines, manometers, etc. Light in weight and may be used safely in apparatus set ups. Fits tubing of 5/16" to 3/16" ID.

DROPPER BOTTLES

With New Improved Caps

Screw-on cap effects tight seal permanently. Drops are small and uniform. By far the best available for laboratory use.

Six sizes, priced from .12 ea. in case (72) lots.



POWDER FUNNELS

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Out of the EDITOR'S BASKET

industrial and nuclear research fields. It is capable of registering one million counts per minute, with counting periods of up to 55 minutes preset in the automatic timer. Discriminator sensitivity and high voltage supply are easily adjusted to suit the requirements of each counting job.

New Literature

● Copies of *Bulletin 340* on Stokes water stills may be obtained on request from the Pharmaceutical Equipment Division of F. J. Stokes Corp., 5500 Tabor Rd., Philadelphia 20, Pennsylvania. The bulletin describes specifications and available accessories for the various stills.

● William J. Hacker & Co., Inc., P. O. Box 646, West Caldwell, New Jersey, offers a new 16 page illustrated catalogue on the new Reichert Research Microscope "Zetopan-pol."

● The Spinco Division of Beckman Instruments, Inc., 1117 California Ave., Palo Alto, California, offers a technical review titled, *An Introduction to Density Gradient Centrifugation*. Chapters cover the following topics: The Density Gradient Principle, Stabilized Moving-Boundary Centrifugation, Use of the Centrifuge, Isopycnic Gradient Centrifugation, Materials Used to Form Gradients, Gradient-Forming Devices, Fractionation Devices, and Applications as well as an extensive bibliography of 76 items.

● Press copies of abstracts of papers presented at the "Fourth Symposium on Temperature" March 27–31, 1961, at Columbus, Ohio, may be obtained from Eugene Kone, American Institute of Physics, 335 East 45th St., New York 17, N. Y.

● Tracerlab, 1601 Trapelo Rd., Waltham 54, Massachusetts, offers five new Tracerlab services described in the following bulletins: *Mercury Inventory in Caustic Soda Electrolytic Cells, Boron Analysis of Industrial Products and Materials, Radium-226 and Radon-222 Analysis, Tracerlab Environmental Survey and Analytical Service and Subsieve Size Radioactive Particle Analysis.*

● A revised edition of *This Is Glass*, a comprehensive story of glass and glass-ceramics, has been published by Corning Glass Works, Corning, New York. The 68-page illustrated booklet reviews the history of glass and details the basic types of glass. The publication describes the expanding role of glass in science, industry, electronics, lighting and the home.

● More then 100 formulations for the use of Aroclor compounds as fortifying extenders and plasticizers in a wide variety of resins are contained in a new technical bulletin available from Mr. Robert Hogan, Monsanto Chemical Co.,

(*Continued on page A340*)

Research

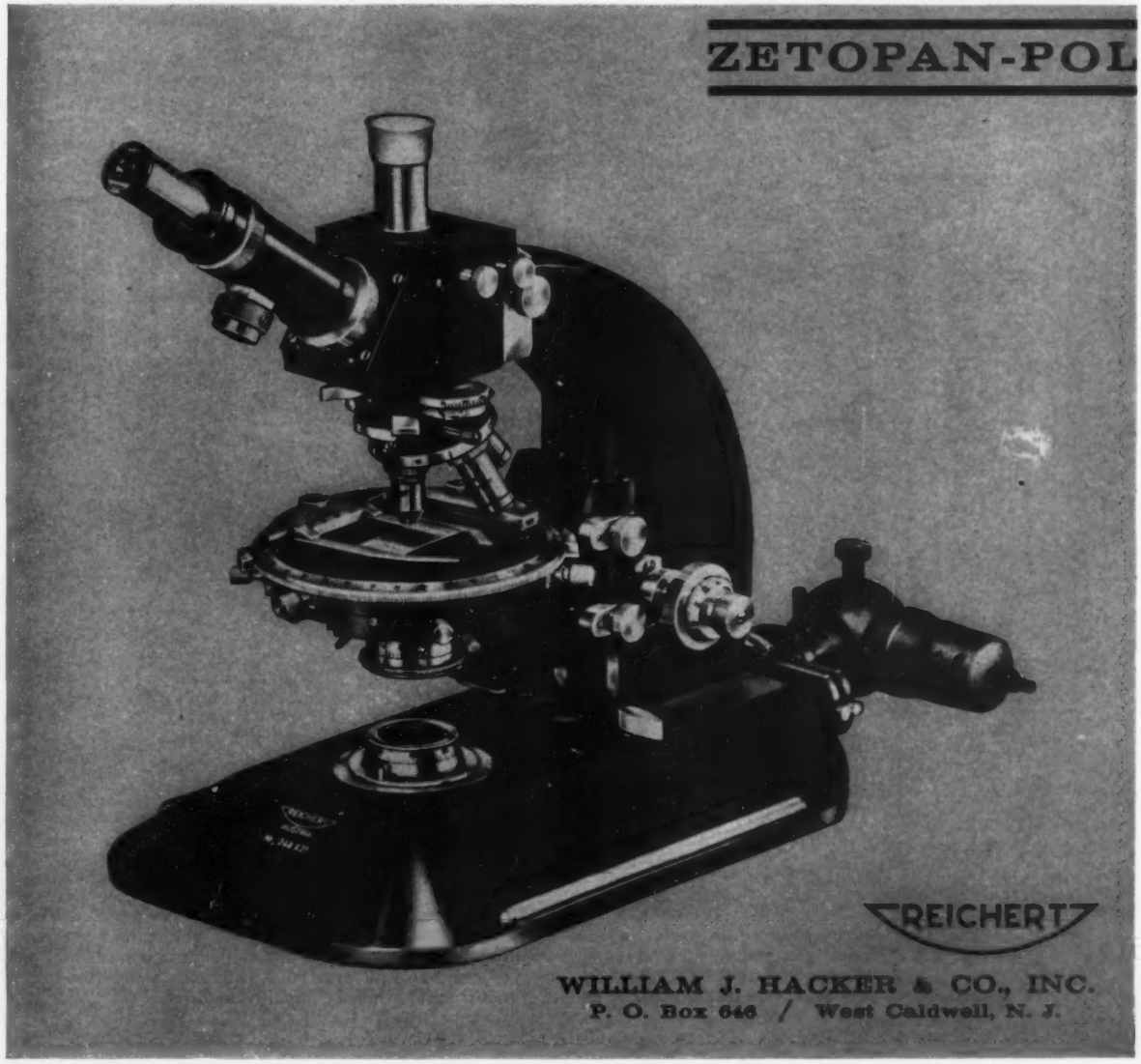
POLARIZATION MICROSCOPY

With the REICHERT

ZETOPAN-POL

The highly specialized field of polarization microscopy requires instrumentation that goes far beyond the general concept of precision. Before investing in a microscope for this work, you must be sure that the degree of accuracy conforms to the closest possible tolerances. The **Reichert** concern, with nearly a century of history, has the experience and skill indispensible for the development of a research polarizing microscope. In releasing the **"Zetopan-Pol", Reichert** created a modern instrument that combines optimum precision with unlimited versatility at utmost working comfort and instantaneous transitions through all phases of light microscopy with photomicrography. Truly an instrument worthy of your consideration!

Polarizing equipment includes: Circular stage, rotatable 360° reading 0.1°, detachable mechanical stage, traversing 20 x 30 mm reading to 0.1 mm, binocular and monocular orthoscopic examination, quick transition from orthoscopic to large conoscopic image by means of built-in swing-out type Bertrand lens, rotatable filter polarizer and analyzer, revolving quadruple nosepiece for individual centering of each objective, sextuple ball-bearing nosepiece on wide range of strainfree objectives, opaque illuminator for instantaneous transition to reflected light.



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GETTING an exacting production-line O.K. is this Fisher Zone Refiner (left). Automatically, it will sweep impurities out of most commercial reagents, upgrade them to well-nigh primary-standard quality. It's representative of many laboratory instruments and appliances only Fisher Scientific makes in its new 116,500-sq-ft plant . . . so that your work can be simpler, faster, surer, safer, or more economical.

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Out of the EDITOR'S BASKET

Organic Chemicals Division, St. Louis 66, Missouri.

● A bulletin just released by Fischer & Porter, 855 Jacksonville Rd., Warminster, Pennsylvania, describes five unique items recently added to its line of laboratory ware.

● A new edition of *Atomic Energy Commission Research Reports*, the semi-annual price list of all unclassified reports of AEC research for sale by the Office of Technical Services, Business and Defense Services Administration, U. S. Department of Commerce, Washington 25, D. C., has just been published.

The 64-page list includes more than 5000 reports in the OTS collection of documents acquired as of January 1961. The new list may be obtained free by requesting *ACE Research Reports Price List No. 35* from OTS, U. S. Department of Commerce, Washington 25, D. C.

● Other books from the OTS are: 60–21172, *Rare Earth Elements*, published by the USSR Academy of Sciences, 356 pages, $3.75. 60–21041, *Survey of Russian Literature for Research on Unstable Chemical Species and the Stabilization Thereof*, 42 pages, $1.25.

● Jarrell-Ash Company, 26 Farwell Street, Newtonville 60, Massachusetts, offers a new grating catalogue covering all plane and concave gratings available.

● Bel-Art Products of Pequannock, New Jersey, announces their new 1961 catalog is now ready for distribution. It features a complete line of plastic ware for science and industry. This 44 page catalog describes, illustrates and gives prices on hundreds of items in various plastics and other materials. Copy available upon request.

● A 12 page discussion and depiction of the latest radiation detection devices based on the use of quartz fibers is presented in Catalog G-13A available from William B. Johnson & Associates, Inc., P. O. Box 415, Mt. Lakes, New Jersey.

● Consultants Bureau Enterprises, Inc., 227 W. 17th St., New York 17, N. Y., offer information concerning the *Bulletin of the Academy of Sciences, USSR, Division of Chemical Science, Fourth Soviet Conference on Electrochemistry*, and other Soviet publications.

●A descriptive *Bulletin No. 773* containing general information, photos, and specifications about the new Beckman Hygromite is now available from the Scientific and Process Instruments Division of Beckman Instruments, Inc., Fullerton, California. The Hygromite, a portable laboratory moisture meter continuously monitors water vapor in gas. Performing with a full-scale accuracy of ±5%, the instrument measures vapor in ppm ranges of 0–10, 0–30, 0–100, 0–300, and 0–1, 000. The Hygromite is designed for use in many control applications, including the monitoring of gas in purge systems, the measuring of moisture in the helium used for precise chromatographic techniques, the monitoring of gas dryers in laboratories, the checking of water content in bottled gases, and the monitoring of natural gas in petroleum research labs and pilot plants.

New Chemicals

◇ Applied Science Laboratories, 140 N. Barnard St., State College, Pennsylvania, has expanded its line of fatty acid chemicals to include carbon-14 labeled high purity materials. The first in this series are linoleic, oleic, stearic and palmitic acids with a specific activity of 4–7 mc/mM. These are available in radio and chemical purities exceeding 99%.

◇ City Chemical Co., 132 W. 22nd St., New York 11, N. Y., offers cobalt selenate and magnesium bromate in experimental quantities.

◇ An inventory clearance sale of 36 tracer compounds labeled with Carbon-14 is announced by Research Specialties Co., 200 S. Garrard Blvd., Richmond, California. Price list and order blank are included in the February issue of the *RSCo Review*, which describes the company's radiochemical products.

(*Continued on page A344*)

CLEANEST CLEANEST CLEANEST CLEANEST CLEANEST CLEANEST

THE WORLD'S FINEST DETERGENT

ALCONOX

Proven the world's finest and most economical detergent for the exacting requirements of Hospital, Medical and Laboratory use.

MEETS HIGHEST U.S. GOVERNMENT SPECIFICATIONS

MORE WETTING POWER!
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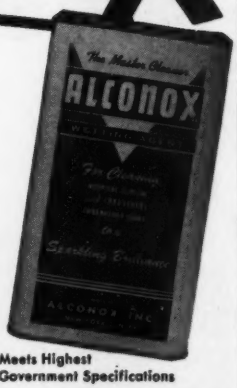
QUICKLY, COMPLETELY SOLUBLE AND RINSABLE!



More effective than any known detergent in powder form or any liquid detergent that costs four times as much!

Meets Highest Government Specifications

Sold Throughout the World by
ALL LEADING LABORATORY, HOSPITAL and SURGICAL DEALERS

Also makers of ALCOJET for all equipment washed by machine and ALCOTABS in tablet form for all pipette washers.

Ask your supplier for a copy of the remarkable Alconox Cleaning Guide which may be reproduced for all your students.

ALCONOX, INC., 853 BROADWAY, NEW YORK 3, N.Y.

Kodak reports on:

how you too can crack the 2500Å barrier...a way you can almost make itaconic anhydride... where a disciple can look for details

Ultraviolet swab

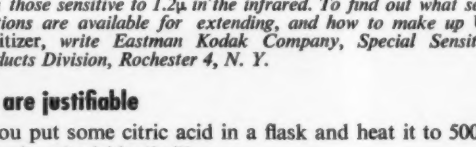
Even the sports pages are carrying help-wanted ads for infrared experts. Infrared is riding high. Let's not forget that at the other end of the visible spectrum the old ultraviolet is still there.

In order to stir up interest in the ultraviolet, we shall show you how to sensitize photographic plates below 2500A, the wavelength down to which all photographic emulsion responds but below which the gelatin of the emulsion starts to intercept the energy so that people don't bother as much as they should with the spectral lines and other interesting phenomena down there.

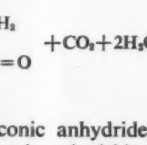
Working thus in the darkroom, you can extend the sensitivity of any of the numerous Kodak Spectroscopic Plates *down to 1000A, even those sensitive to 1.2μ in the infrared. To find out what sensitizations are available for extending, and how to make up* U-V sensitizer, *write Eastman Kodak Company, Special Sensitized Products Division, Rochester 4, N. Y.*

We are justifiable

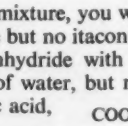
If you put some citric acid in a flask and heat it to 500°C, itaconic anhydride distills over.



If you happen to want some itaconic anhydride, this method will exasperate you. The itaconic anhydride keeps rearranging into citraconic anhydride,



If you redistill the crude mixture, you wind up with good quality citraconic anhydride but no itaconic anhydride. You can treat the citraconic anhydride with 25% nitric acid, which restores a molecule of water, but now you have the *trans* form called mesaconic acid,



Still no itaconic anhydride.

At this point you order *Itaconic Anhydride* from us as Eastman 8291. We have a chemist who found out what changes to make in the published method for changing commercial itaconic acid to itaconic anhydride so that it would work. You owe him no salary for the time he was finding this out. Nor are you responsible for his professional and intellectual development. All you want is a little itaconic anhydride. Why do you want it? Goodness knows. Goodness knows why *most* of the compounds in our catalog are wanted. But, boy, are they wanted! Business has never been better. Drives us frantic.

You can't do your part unless you have a copy of "Eastman Organic Chemicals, List No. 42." It comes from Distillation Products Industries, Rochester 3, N. Y. (Division of Eastman Kodak Company). Many laboratory supply dealers, along with us, stock the chemicals.

Small print

This little file holds some 10,000 unabridged pages of technical reports of the French Atomic Energy Commission. The lady who lives in the house across the road may find this astonishing. Your boss may be astonished. Even you may be astonished. But to the reasonably alert librarian the micro-opaque card idea is old hat. Anything we can tell you about it your librarian can tell you better.* We merely draw attention to the following accretions to the available micro-opaque literature:

- **All the unclassified scientific reports released by the U. S. Atomic Energy Commission.**
  Even reduced 20× as they are in micro-opaque form, the complete set published to date would fill 250 boxes like the one above. The indexing mechanism for this incredible mass of information is *Nuclear Science Abstracts*, a periodical sold by the Superintendent of Documents, Washington 25, D. C.

- **The 1st Decennial Index to *Chemical Abstracts*, the brilliant chemical years 1907 to 1916.**
  Contains the roots of many a chemical concept since proliferated beyond the scope of a single mind. On some 60 3" x 5" cards sold by the American Chemical Society (1155 16th St. N. W., Washington 6, D. C.).

- **All the meteorological data gathered for the International Geophysical Year.**
  Purpose of whole shebang was to gather lots of data, remember? Here they are, ready to make use of. Ask the World Meteorological Organization (IGY Meteorological Data Centre, 1, Avenue de la Paix, Geneva, Switzerland).

- ***Justus Liebigs Annalen der Chemie* from 1832 to 1958 and *Berichte der Deutschen Chemischen Gesellschaft* from 1868 to 1958.**
  The New Testament comprises four Gospels; the science of chemistry seems to be founded on only three gospels, less influential spiritually but vastly more voluminous. Microprint overcomes the voluminousness but accomplishes nothing spiritually. The third gospel, *Beilstein*, got the treatment earlier. Microcard Editions, Inc.

- ***The First Six Million Prime Numbers.* 1 (controversial) to 104,395,289.**
  Result of a 4-day holiday weekend with a large computer and nothing better to do than a favor for mathematicians working in number theory. Microcard Editions, Inc.

For any sustained use of micro-opaques, you need a micro-opaque reader. Ten years ago they were rare. Today the central research library that lacks one is rare. Any scientific discipline that needs to communicate large masses of data to a limited number of its disciples should consider microprint. For suggestions on how to proceed, write Recordak Corporation, 415 Madison Avenue, New York 17, New York (Subsidiary of Eastman Kodak Company).

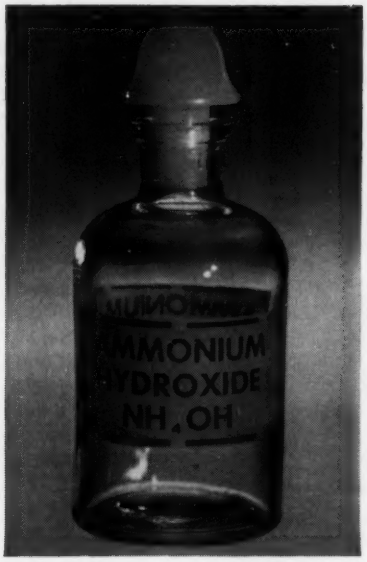
*The reason *we* try to tell you is that we want to sell the raw photographic materials on which microprint cards are printed. We also want to sell microfilm. The librarian can tell you about *that*, too. A new conventional-sized reference, "Guide to Microforms in Print" ($4, Microcard Editions, Inc.), summarizes everything available.

Kodak

This is another advertisement where Eastman Kodak Company probes at random for mutual interests and occasionally a little revenue from those whose work has something to do with science

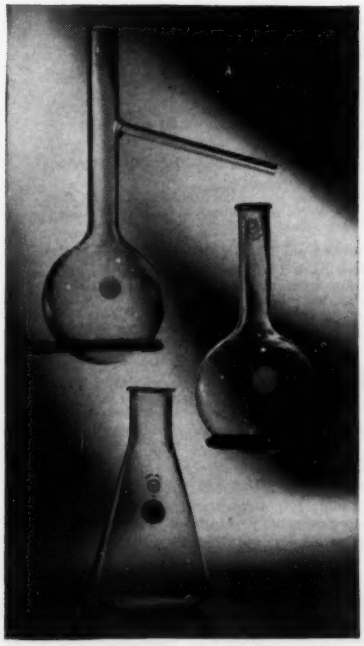
Why PYREX® labware is a good b

Machine-made beakers. Each one with walls as heavy and uniform as every other—for maximum strength. For a few pennies more than the cost of the standard No. 1000 beaker, you can get the new No. 1002 with white enamel approximate graduations.

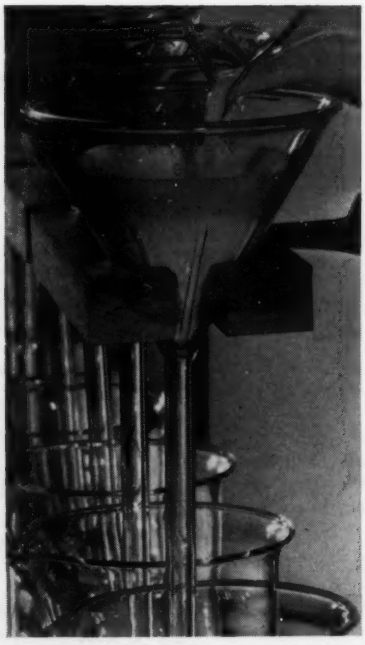


Our No. 1552 reagent bottles make good reading. They're smartly labeled front and back in permanent green on a white enamel background. Ideal for divided-bench use. The bottles won't cloud, the polyethylene stoppers won't stick.

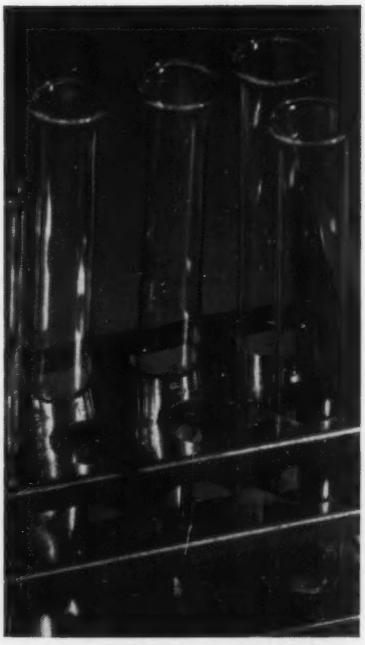
The No. 3075 cylinder is designed for students. Its detachable hexagonal plastic base won't break, discourages the cylinder from tipping and rolling. Cylinder top and spout are heavily reinforced. Sharp, white graduations.



Flasks must take knocks and bangs, quick heating and quick cooling. PYREX boiling, distilling, and Erlenmeyer flasks provide over-all strength for safety. They're designed to conduct heat quickly and evenly.

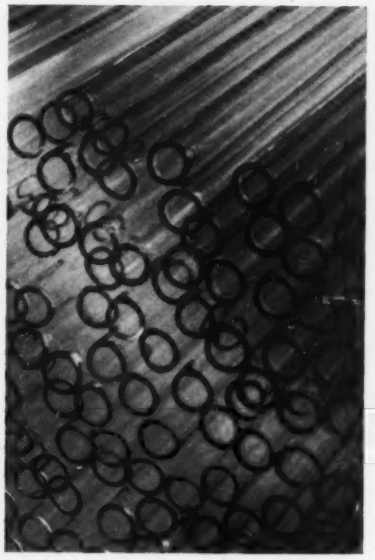


Your students get faster, more complete filtration with Nos. 6160, 6180 funnels, because of filtering grooves pressed into the cone wall. Pressed construction also builds strength and makes for an accurate angle for the filter paper.

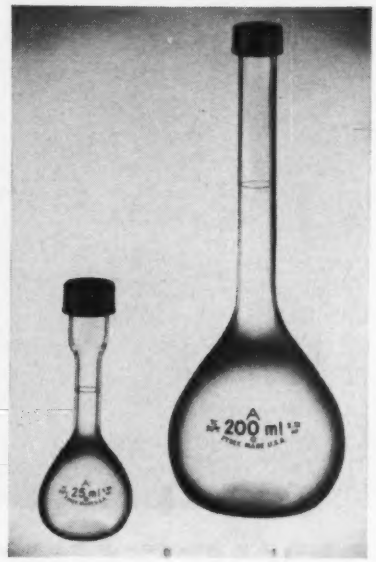


Machines make our test tubes stronger, especially at top and bottom hazard points. The tubes are reinforced with a bead at the lip to resist chipping. Bottom radii are machine-uniform in strength, dependability, thermal safety.

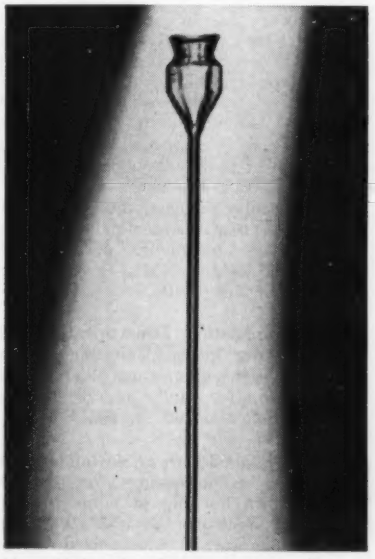
buy...the old-fashioned kind



Our No. 0088 soft glass tubing and rod work easily for your students over a Bunsen burner, and give them improved chemical durability, too. For heat-resistant applications, we recommend PYREX tubing and rod.



You get Class A accuracy at a real saving in the No. 5650 volumetric flask. You also get the convenience of a screw cap. The plastic cap won't leak or freeze on. There's no stopper to fall out and break. Priced lower than glass-stoppered flasks.



New thistle tube design prevents rolling-off accidents. The square molded design of the No. 6440 gives added strength. Extra glass at the tube-body seal means longer life.

Our molded No. 9985 watch glasses are heavier, stronger than blown types. Their rounded, heat-formed edges increase their strength. Uniform curvature makes stacking easy. You can use them as evaporating dishes, too—they take direct heat.

SCIENCE teachers across the land should always look for bargains in scientific apparatus. But we ask you to keep in mind just what a bargain is.

A graduated cylinder that breaks is no bargain no matter what its price.

A reagent bottle whose markings become illegible is no bargain.

A bargain is when you get *more* than you expected for your money. If you haven't been using the PYREX labware shown here, then we can show you bargains . . . ten of them.

Our bargains show up as such when you take inventory at the end of the semester. That's when you find that our ware tends to last longer than others'. That's when your replacement costs are reduced.

Our bargains show up every time a student uses our ware. He finds out we've allowed for his inexperience. He finds out we make thicker, safer, longer-lasting ware.

Our bargains show up when you find that you can fill all your lab glassware needs with one order and take advantage of quantity discounts.

Check with your lab supply dealer the next time you go bargain hunting.

We have put together a compact new guide to PYREX labware for schools, which is yours for the asking via the coupon.

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Please send me the new "Science Teacher's Guide to Laboratory Glassware."

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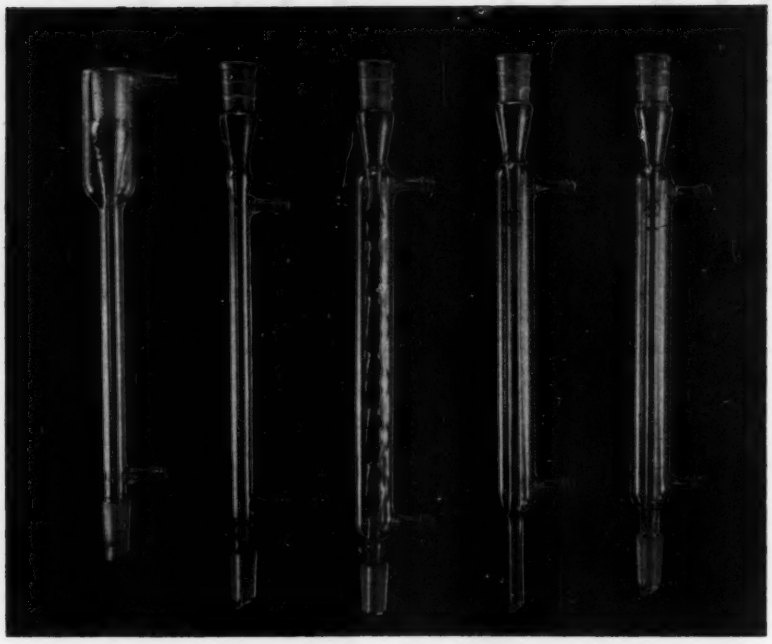
PYREX® laboratory ware ... *the tested tool of modern research*



ACE CONDENSERS re-designed for greater efficiency

Ace condensers have been re-designed to operate more efficiently than ever before. "No Hold Up" condensers (shown above) are of an approved drainage design, especially useful for straight run distillations. The inlet taper is at the proper angle to provide complete drainage with a standard 75° take-off arm. Extra care is also exercised to see that seals do not cause hold-up. Hose connections are placed on the same side (opposite the drip) providing a clean work space under the condenser in the "horizontal" position. No air is trapped since the inlet is lower than the outlet.

The new style drip tip is unconstricted, permits full use of the condenser surface and eliminates choking. Hose connections are designed for strength and utility. The ends are beaded to absorb impact, and a large head is provided as a grip. The hose does not slip off as with uniformly tapered beading.

The wide variety of Ace condensers is described in Ace Catalog 60. If you do not have a copy of this comprehensive catalog, please ask Dept. J for your copy.

ACE GLASS
INCORPORATED
Louisville, Ky., Vineland N. J. Springfield, Mass.

Out of the EDITOR'S BASKET

Miscellany

★ "Science for Science—The Story of the Scientific Laboratory Furniture Industry" is the title of a new 35 mm color, sound film-strip available on arrangements from the Laboratory Equipment Section, Scientific Apparatus Makers Association, 20 N. Wacker Dr., Chicago 6, Illinois.

★ Arizona State University will offer the first annual course in Infrared and Ultraviolet Absorption Spectroscopy on campus from August 7–11, 1961. Particularly designed for chemists and others from industrial laboratories which make use of spectrophotometric equipment, this intensive course of lectures and practical laboratory work serves to train personnel to staff these installations. For complete information, please write to Dr. Jacob Fuchs, Director, Absorption Spectroscopy, Arizona State University, Tempe, Arizona.

★ Technical Aid Service, Inc., 1500 W. Third Ave., Kingsview Bldg., Columbus 12, Ohio, is now offering a unique service especially tailored for management and research and development staffs of electronics, petroleum processing, petrochemical, chemical, pharmaceutical, and related firms. The service entails the reduction of technical literature to easily understood digests of basic principles. These digests are integrated into an intelligent retrieval system.

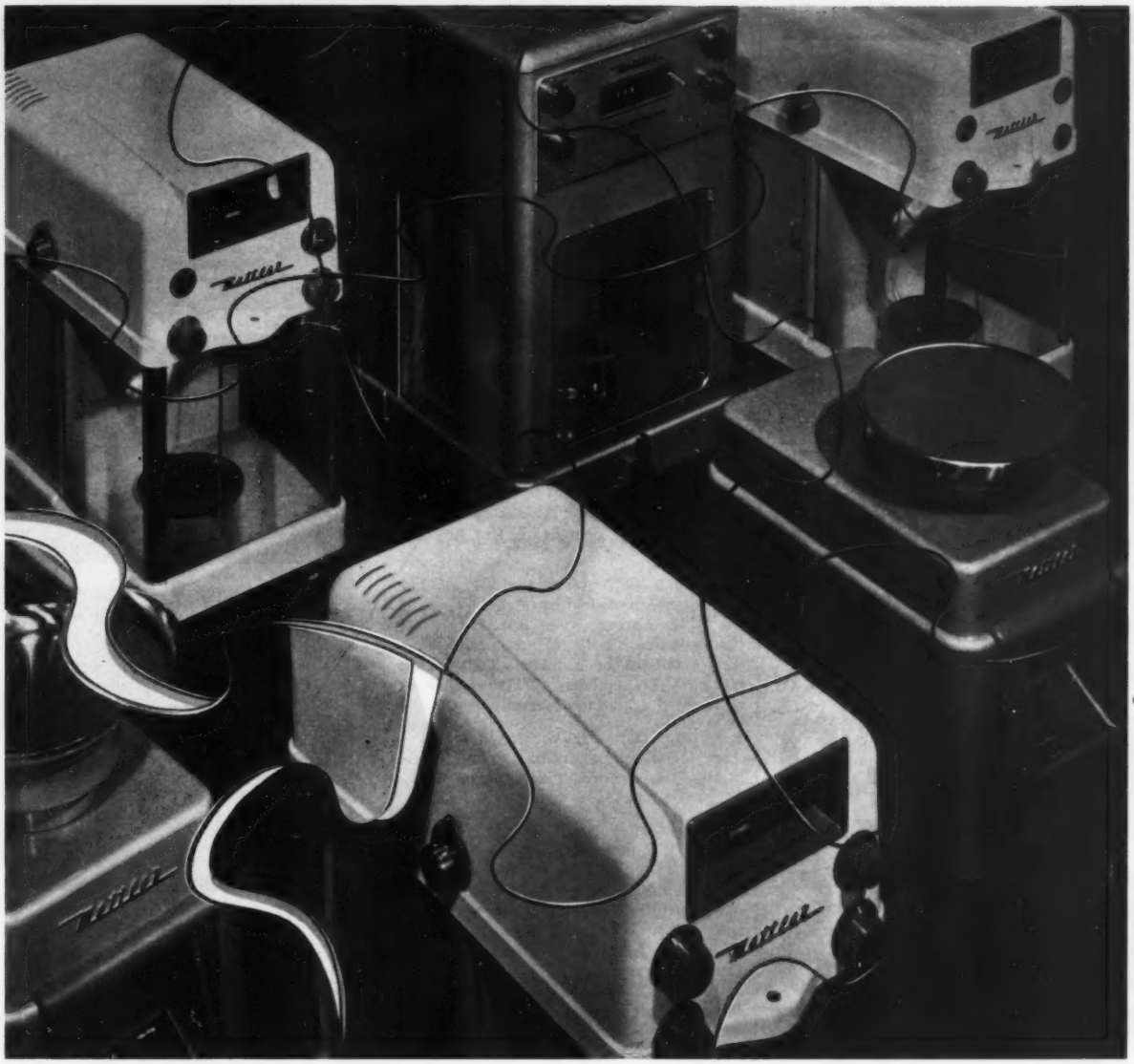
★ The opening of a new Analytical Service Center has just been announced by Ridgefield Instrument Group, Schlumberger Corp., Ridgefield, Connecticut. In making the announcement, A. Russel Aikman, Director of Marketing for the Ridgefield scientific instrument and electronics firm, pointed out that the new Center is believed to be the first analytical service facility in the country offering all three of the relatively new radio-frequency spectroscopy techniques of Spin-Echo NMR, Wide-Line NMR, and Electron Spin Resonance (ESR).

★The Circulation Department, Audio-Visual Center, Indiana University, Bloomington, Indiana, offers a new film bibliography, "Films for Junior and Senior High School Biological and Physical Sciences."

★ The National Bureau of Standards has developed gallium alloys for the low-temperature bonding of wires to heat-sensitive electronic devices. These alloys, which are soft when mixed at room temperature, resist temperatures up to 900°C after hardening. It was also found that they could be used to "cold solder" certain ceramic and metallic surfaces.

★ Thirteen young scientists are now conducting advanced basic studies as Postdoctoral Research Associates at the

(*Continued on page A346*)



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Out of the EDITOR'S BASKET

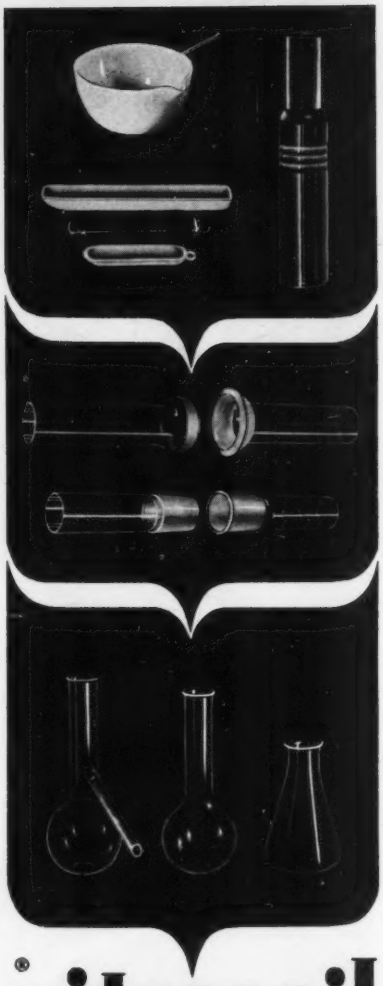
National Bureau of Standards. The associateships, sponsored jointly by the National Academy of Sciences-National Research Council and the Bureau, give young scientists an opportunity to pursue a year's study and research in their fields of competence, in close association with a Bureau staff member whose work in the field is well established. Applicants for the NRC-NBS Associateships must in all cases have completed the requirements for a doctorate in one of the physical sciences, and must have received their Ph.D. degrees by the time they enter upon the associateship. They also must be United States citizens. Application is made directly to the National Academy of Sciences in response to an announcement, distributed by the Academy annually in November to all universities granting Ph.D. degrees in the physical sciences.

★ Volume 29 Number 1, 1961, of *The Laboratory*, published by Fisher Scientific Co., 711 Forbes Ave., Pittsburgh 19, Pennsylvania, tells of research being carried out at the Montreal Neurological Institute on epilepsy. The article is entitled "Storm in the Brain."

★ "Snow Camping with Nylon" is a story for the rugged outdoors man found in the March-April, 1961, *DuPont Magazine*.

★During the 1961 Summer Session Columbia University's School of Library Service will offer again a course on *Scientific and technical abstracting and indexing* (LS s132). The course will be taught by T. E. R. Singer, formerly Chemistry Librarian at the New York Public Library and now a private consultant in the field of technical information. It will provide an analysis of various uses to which scientific and technical abstracts are put, the types of abstracts suitable for particular uses, the techniques of indexing abstracts, and instruction and practice in abstracting. There will be a number of lectures by experts in major scientific fields on their technical terminologies. Applications may be obtained from the School of Library Service, Columbia University, New York 27, N.Y.

★Applications are being accepted for AEC Reactor Courses at Oak Ridge National Laboratory next fall. Two courses–reactor operations supervision and reactor hazards evaluation–will be offered. Applicants should possess a bachelor's degree in chemistry, physics, metallurgy, mathematics, engineering physics, or in aeronautical, chemical, civil, electrical, mechanical, metallurgical, general or nuclear engineering. International applicants may apply through their respective embassies or legations to the U. S. Dept. of State. U. S. Citizens may apply to the Director, Division of International Affairs, U. S. Atomic Energy Commission, Washington, D. C. The deadline for submitting applications is June 15.



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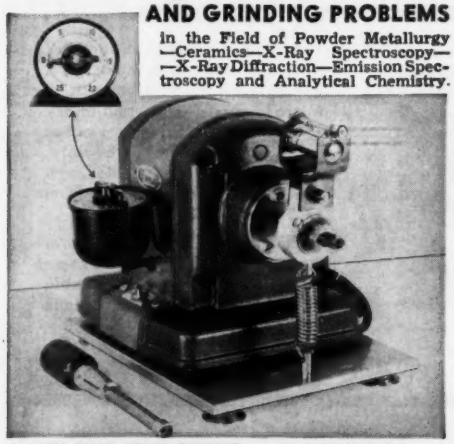

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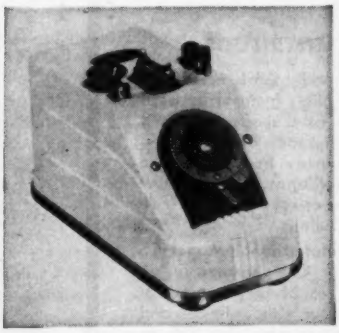
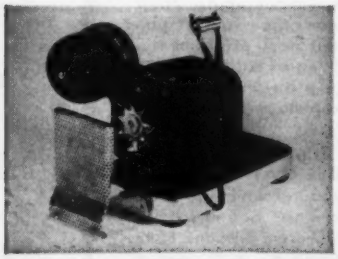
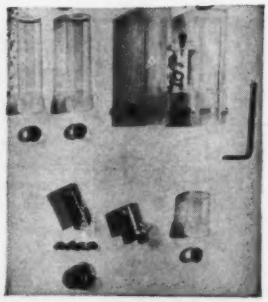


5A—Wonder Electric Mortar—the action is reciprocating in the form of a figure 8 swung through a 6 ½° arc at 3200 RPM, the ball pestle then strikes the end of the vial some 2000 times in ten seconds. Can be run continuously for 5 minutes (and this depends on the load) with a rest period between the 5 minutes to cool the motor completely.



3A—Model with Fan and 1 hour timer—same type of motor and action as 5A Model but this 3A can be run for 20-30 minutes with cooling off periods between to cool the motor.



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3113 Adapter, for ½″ dia. x 1″ long vials.
3111 Vial, ½″ x 1″ polystyrene with cap.
3112 Ball-pestle, clear plexiglas, ½″ dia.
3115 Adapter for ½″ dia. x 2″ long vials.
3116 Vial, ½″ x 2″ polystyrene with cap.
3113 Adapter for ½″ dia. x 1″ long vials.
3114 Vial, stainless steel ½″ x 1″ with ball-pestle ¼″ dia.
3117 Vial, tool steel (hardened) ½″ x 1″ with steel ball-pestle ¼″ dia.
3118 Vial, agate 9/16″ dia. x 13/16″ long 2 ml capacity with agate ball-pestle ¼″ dia. (Requires 3115 adapter).

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- Model N heater is equipped with a 1" power cord and male Hubbell twist-lock connector. It requires a 2-wire standard attachment cord, 3' long, extra at $1.00.
- Model N-3 heaters have a 3-wire, 1" power cord with a Hubbell twist-lock connector. Add $1.25 to above prices for a Model N-3 heater. Requires 3-wire attachment cord extra at $2.75; state whether male plug hot prongs are parallel or angled.
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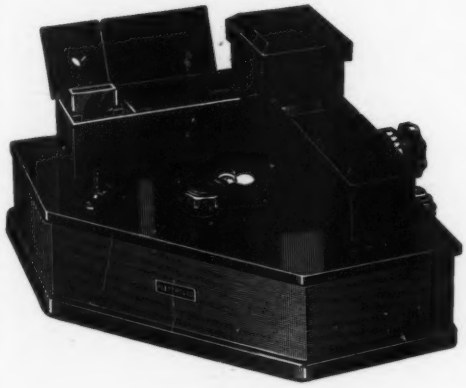

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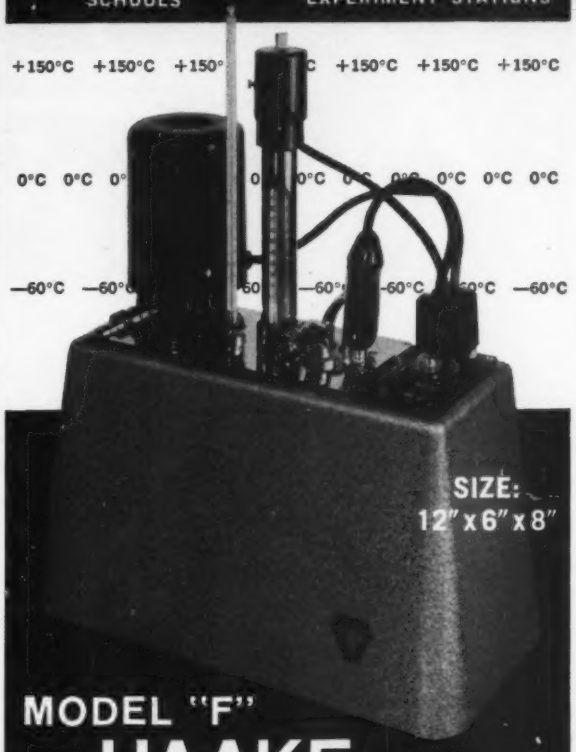

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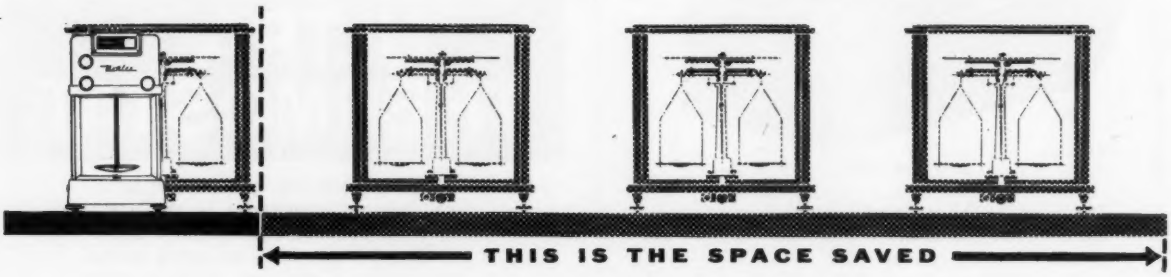

The diagram is based on the conservative assumption that one Mettler balance does the work of four equal-arm, undamped student balances.

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CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** Kings College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

Solubility of Sulfur: An Undergraduate Research Project

See BROOKE, M., *J. Chem. Educ.*, **28,** 434–435 (1951).

The solubility of sulfur in volatile solvents is determined by placing an excess of sulfur in the selected solvent in a flask fitted with a reflux condenser. At various selected temperatures, after equilibrium has been established, aliquots are withdrawn and weighed, the solvent evaporated, and the residual sulfur weighed. For non-volatile solvents, a weighed quantity of sulfur is placed in a weighed quantity of solvent and the temperature raised until all the sulfur is dissolved. The temperature at which the mixture becomes turbid, as the solution is cooled, is noted.

Questions:

The procedure described in this article can be used for many solute-solvent systems. Select any solute and solvent and determine the solubility of the solute in the solvent as a function of temperature. Is there any relationship between the solubilities of a selected solute in a series of homologously or isomerically related solvents?

For precise work the solute and solvent selected should be known to be pure. Prepare pure solute and solvent, check their purity by suitable analytical techniques, and measure the solubility characteristics of this solute-solvent pair.

In comparison with the total possible number of solute-solvent pairs, data on solubilities in the published literature are quite incomplete. After a thorough search of the literature, select a solute-solvent pair for which there are no data or for which the data are incomplete and determine the solubility characteristics of this new solute-solvent pair. Materials of analytically determined purity should be used and the necessary technique should be acquired by performing the appropriate operations with a solute-solvent pair whose solubility characteristics are known, repeating until your data conform with those in the literature, before proceeding to the new pair. Any literature search to identify gaps in the published literature could begin, but should not end, with *Chemical Abstracts*. Precise data on new solute-solvent pairs might well be publishable.

Determination of the Density of Oxygen Gas

See FIEKERS, B. A., *J. Chem. Educ.*, **31,** 139–140 (1954).

Oxygen, supplied from a pre-weighed "Oxybomb," is collected over water. The volume, pressure and temperature of the collected gas are measured. These data, together with the weight of the partially exhausted Oxybomb, can be used to calculate the density of oxygen under the pressure and temperature at which it was collected. (An Oxybomb is a small 2.5 in. × 0.62 in. cylindrical metal cartridge filled with oxygen under pressure. A needle valve which fits the neck of the cartridge is used to control the amount of gas removed from the cartridge.)

Cartridges of other gases are available, although special needle valves not commercially available would have to be designed and constructed for some of these.

Questions:

What is the molecular weight of oxygen?

Using oxygen, evaluate R, the ideal gas constant.

How many molecules are there in one mole of oxygen?

Determine the molecular weight of a gas other than oxygen.

Using a gas other than oxygen, determine the value of R or of Avogadro's number.

Molecular Association Equilibria from Distribution and Related Measurements

See DAVIES, M., AND HALLAM, H. E., *J. Chem. Educ.*, **33,** 322–7 (1956).

Many compounds are soluble in more than one solvent. For example, acetic acid is soluble in water, in benzene, and in other liquids. If an aqueous solution of acetic acid is placed in a vessel containing some benzene, the acetic acid dissolves, to some extent, in the benzene. After a suitable period of time, an equilibrium is established between the acetic acid in the water layer and in the benzene layer:

$$HOAc_{\text{in water}} \rightleftarrows HOAc_{\text{in benzene}}$$

The above equation is incomplete in that it does not indicate the ionization of acetic acid in water solution, nor does it indicate the molecular association of this solute in benzene. This equation is closer to the truth:

$$2H_3O^+ + 2OAc^- \rightleftarrows 2HOAc_{\text{in water}} \rightleftarrows (HOAc)_{2\text{in benzene}}$$

However, data obtained from laboratory experiments indicate that this equation, also, is not completely accurate, particularly with respect to the species which exist in the benzene solution.

The data are obtained by adding benzene to an aqueous solution of acetic acid and mixing vigorously. After the layers have separated upon standing, aliquots of both layers are titrated with a base of known concentration. (Details can be found in any laboratory manual of physical chemistry. The liquids should be at a known, constant temperature, and should be maintained at this temperature until the aliquots are withdrawn.)

Mathematical details relating to the inaccuracies of the above equations are discussed in the article by Davies and Hallam.

Questions:

Is acetic acid dimeric in benzene, or does it exist in some other form in this solvent?

In what form does acetamide exist in chloroform solution?

Using other solutes and solvents, determine the degree of association of the chosen solute in the selected solvent.

(This investigation is particularly suitable for the student who is interested in the relationship between mathematics and chemistry.)

Gas-Phase Chromatography: A Class Experiment

See BRENNAN, D., AND KEMBALL, C., *J. Chem. Educ.*, **33**, 490–492 (1956).

As an analytical tool, gas chromatography can be applied both to gaseous mixtures and to mixtures of volatile materials. With sufficient attention to detail, the data that are obtained can be interpreted quantitatively. This article describes the construction and operation of a gas chromatograph; two articles immediately preceding[1] discuss the principles.

The chromatographic column can be filled with any one of the several available materials now on the market instead of the specific material recommended. The device immediately on the right of flask B_2 in Figure 1 is a vacuum pump.

[1] CASSIDY, H. G., *J. Chem. Educ.*, **33**, 482 (1956); LOTZ, J. R. and WILLINGHAM, C. B., *J. Chem. Educ.*, **33**, 485 (1956).

Questions:

Should peak heights or peak areas of a chromatogram be used to determine the composition of a mixture?

What factors determine the optimum temperature of operation of an adsorption column?

Does the precision or the accuracy of an analysis, or both, depend upon the rate of flow of gas through a gas chromatograph?

Is distilled cider vinegar merely an aqueous solution of acetic acid?

The ethyl alcohol content of most liquid flavoring agents is given on the label of the bottle. Can you verify such a statement?

Is the efficiency of an adsorption column for each component of a mixture of hydrocarbons a linear function of the molecular weight of each hydrocarbon?

A Quantitative Sodium Flame Test

See KIPLINGER, C. C., *J. Chem. Educ.*, **28**, 641 (1951).

An inexpensive spectroscope is modified by the use of two pieces of polaroid to serve as a simple spectrophotometer. One piece of polaroid is placed between the prism and the light source; the other is placed in the eyepiece in such a way that rotation of this piece can be indicated by a pointer extending in front of a protractor scale. Solutions containing sodium ion are fed, by a filter paper wick, into a burner flame. The angle of rotation of the polaroid which is necessary to "extinguish" the emitted light is measured on the protractor. This angle is an approximately linear function of the sodium ion concentration, up to about 0.1 molar.

Questions:

Kiplinger mentions certain precautions: the height of the burner flame must be kept constant; if crystals appear on the paper wick, the data are useless, etc. Can you modify this procedure so that it will be less subject to error and easier to obtain reproducible results?

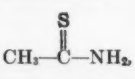
Kiplinger states that the amount of sodium present as an impurity in certain reagents was found to be greater than that indicated as the maximum amount on the labels of the bottles containing these reagents. If true, this is distressing. Can you confirm this result?

Is it possible to use this method for the quantitative determination of other ions, such as potassium, or calcium, or boron?

Thioacetamide as a Sulfide Precipitant in Qualitative and Quantitative Analysis

See GUNNING, H. E., *J. Chem. Educ.*, **32**, 258–259 (1955).

Aqueous solutions of thioacetamide,



hydrolyze rapidly at temperatures above 80° C, forming hydrogen sulfide and other products. Cations which form insoluble sulfides will precipitate as sulfides in a hot solution of thioacetamide. Hence, thioacetamide can be used in qualitative analytical procedures instead of gaseous hydrogen sulfide. No essential change in the analytical procedure is necessary, and the elimination of poisonous, malodorous hydrogen sulfide constitutes an additional advantage.

Because of the very slight solubility of many sulfides, it would seem that quantitative analytical determinations of many different substances could be based upon the precipitation of the constituents as sulfides. When hydrogen sulfide is used, this procedure is not practical because sulfides so formed are often partially colloidal and not completely separable from the liquid media in which they are formed. The same sulfides, precipitated by hydrolysis of thioacetamide, are not colloidal; this procedure can be used for quantitative analytical determinations.

Questions:

Antimony trichloride is soluble in concentrated hydrochloric acid. When sufficient water is added to this solution a white precipitate, probably SbOCl, is formed. Comparison of the calculated percentage of antimony in SbOCl with that found by analysis of the precipitate would serve to confirm or deny the supposed identity of the precipitate. Is SbOCl the correct formula for this precipitate?

Type metal, used by printers in Linotype machines, is an alloy of lead, antimony, tin, and sometimes one or two other metals. This alloy is melted and kept molten prior to casting type; as a result, some oxidation occurs and the composition of the alloy changes. This change is called "dross deterioration." Obtain a sample of used type metal from your local printer. Determine its composition and compare with the original composition of the type metal, as furnished by the type metal supplier. Which component of type metal alloy is preferentially subject to oxidation?

Two different kinds of questions, one relating to a problem that is chemical in nature, and one directing attention to analysis, are given above. Thioacetamide can be used in the analysis of many other compounds and mixtures. From your own experience select a chemical or analytical question which can be answered by using thioacetamide as an analytical tool and set out to find the answer. Examples of a few more such questions are: Does a chemical change occur when silver chloride is exposed to light and thereby becomes darker in color? How much nickel metal is present in a nickel (5¢) coin? What is the thickness of the tin coating on a "tin can?" Different types of solder melt at different temperatures; are these differences in melting points related to differences in composition?

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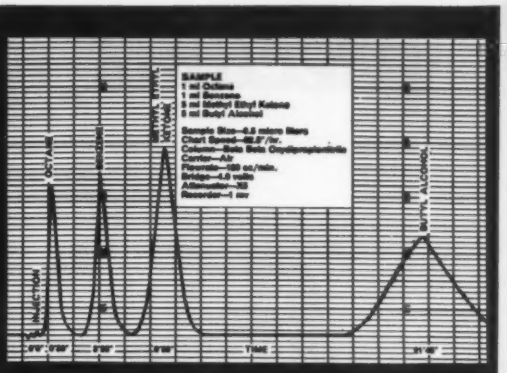

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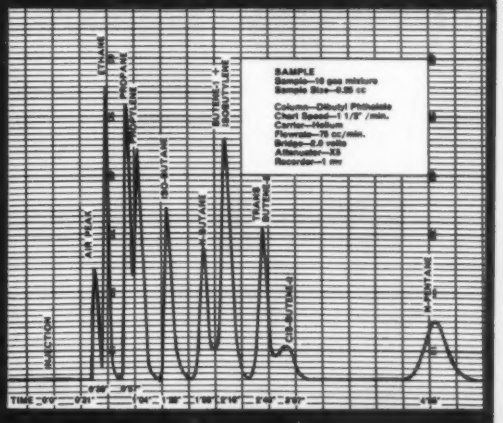

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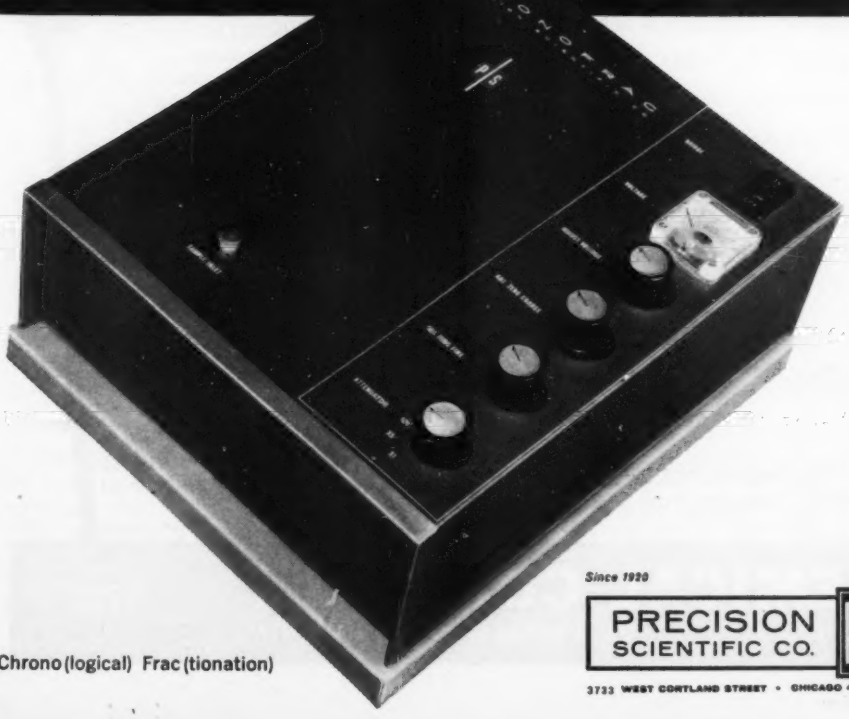

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DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5" X 8" CARDS

TRANSITION TEMPERATURE IN IRON

A Chem Ed TESTED DEMONSTRATION

Rewritten and adapted from: Paul Flinn, "The Physics of Metals" in *Saturday Science*, edited by Andrew Bluemle, E. P. Dutton and Company, Inc., New York, **1960,** by Wayne Taylor, Michigan State University

Checked by: Joseph E. Bowles, Michigan State University

DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5" X 8" CARDS

PREPARATION

Secure approximately one meter of No. 20-gauge iron wire (stove-pipe wire). Mount horizontally with clamps between two support rods. Position meter stick vertically behind the center of the suspended wire so that expansion and contraction may be measured. Attach output of 110-v 15-amp variable transformer across the suspended wire.

DEMONSTRATION

The output voltage is gradually increased until the wire becomes bright red. This point should be beyond the first color change observed. At this point the switch is opened. Close observation will reveal an immediate contraction followed shortly by momentary expansion, then further gradual contraction. The reverse sequence may then be observed by closing the switch. It should be noted that the temperature at which the effect is observed is somewhat critical, hence careful manipulation of the current and initial observation are necessary. Once the correct temperature is determined the effect is quite obvious and may be easily observed as the switch is opened and closed.

REMARKS

The body-centered cubic structure (at room temperature) changes to face-centered cubic structure above 910°C. The face-centered cubic structure has closer packing than the body-centered cubic structure. The change in structure produces a change in volume that in turn is reflected by the obvious change in length.

CONDENSATION OF NOXIOUS GASES

A Chem Ed TESTED DEMONSTRATION

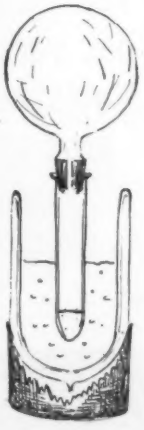
Submitted by: R. B. Escue, North Texas State College, Denton
Checked by: J. R. Brandou, Michigan State University, East Lansing

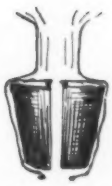
PREPARATION

Introduce the larger end of a one-holed rubber stopper into the neck of a large balloon so that the mouth does not obstruct the hole. By holding the stopper, the opening may be butted to the exit of the compressed gas supply during the filling operation. Grasp the neck of the balloon and introduce the stopper into a test tube which makes a snug fit without removing the balloon from the stopper.

DEMONSTRATION

Place the test tube with attached inflated balloon into a cooling mixture capable of liquefying the gas at atmospheric pressure. After the balloon collapses, remove the unit from cooling mixture for display and watch balloon fill as the gas boils.





REMARKS

Noxious gases can be condensed without use of a fume hood and allowed to vaporize with no discomfort or danger. If desired, the balloon may be removed and refilled while the test tube remains in the cooling mixture. This will allow a larger volume of liquid to be displayed. Sulfur dioxide or ammonia may be condensed in a dry ice-isopropyl alcohol bath. With liquid nitrogen, argon may be frozen, melted (−189.2°C), and boiled (−185.7°C) within a 5° range. Small samples of oxygen may be liquefied in this manner for other demonstrations.

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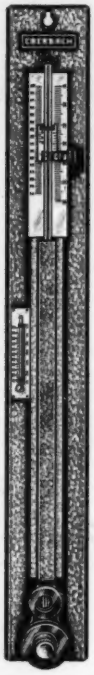

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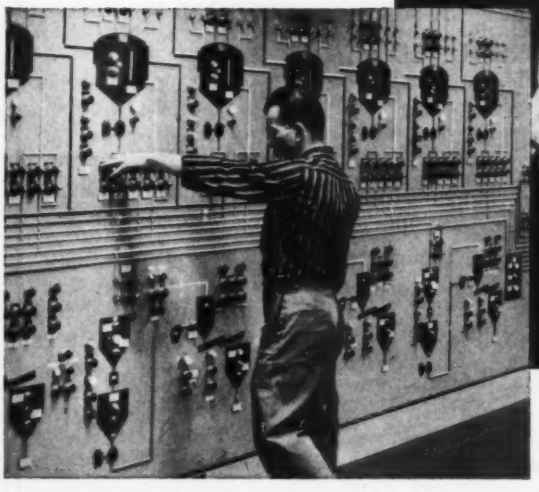

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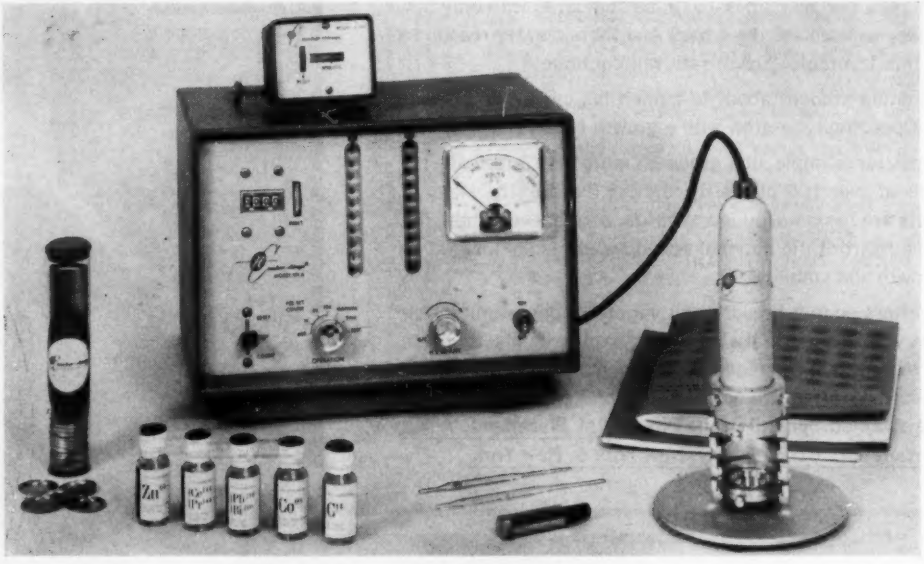

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ChemEd

EDITORIALLY SPEAKING

The data in the committee report which evaluates the status of training students in the use of chemical literature (see page 273, this issue) reveal a near-unanimity on the opinion that such training is essential. This comes as no surprise to any thoughtful educator who realizes what is happening to the chemical literature. We have heard with rather startling frequency the comment that often a research organization finds it cheaper to run the chance of repeating research than to discover via the literature whether work has been done before. Usually this opinion is expressed to emphasize the growing complexity of the literature and the need for developing machine methods of information retrieval.

Nevertheless, no chemist whose business is training the new crop of chemists should let this pass without a twinge of conscience. Does the average chemists' training leave the impression that the literature is an impenetrable mystery? and that trying to probe it is not worth the cost in time and effort? We hope not!

It is essential that every chemist realize that he has two sources of information available to him: the literature *and* the laboratory. Familiarity with both and a working knowledge of the techniques of operating in both are equally fundamental.

The complete text of the report (available on request from the chairman, Professor M. G. Mellon, Purdue University, Lafayette, Indiana) gives some interesting detail in support of the numerical summaries. We note that nearly 97% of the institutions attempt some kind of instruction in the use of the literature. Of these, 40.6% have formal courses which, with very few exceptions, are taught by chemically trained instructors. The use of various means other than formal courses to accomplish this training is reported by 56%.

About two-thirds of the formal courses use a textbook. The course is prescribed in various years, from sophomore to graduate level. Though the nature of the instruction varies widely, lectures and problems are included by most. The course consistently follows the student's acquisition of some facility with foreign language. The proponents of the formal course generally express enthusiasm for the plan; nearly two-thirds require it of all degree candidates. They quote many letters from former students stating that although the course was one of the "toughest," it has proved to be one of the most valuable. One proponent points out that the course has opened such new vistas to students that usually at least one a year decides to make a career of working as a literature chemist.

When no formal course is offered, a variety of plans are used to accomplish the same purpose. Usually two or more instructors require acquaintance with the literature in the subject matter of a course. Although this method admittedly may leave gaps in the student's familiarity with the contents of the library, its advocates point out that its effectiveness rests on the practicality and pertinence to the student's immediate chemical problems. Some laboratory courses demand literature consultation as a first step; invariably research problems require it. The open-book or open-library type of examination is often used to simulate the kind of problem solving the student will find necessary after he graduates.

The kinds of literature sources made use of by students in the "non-course" institutions were investigated. As can be expected, *Chemical Abstracts* is universally consulted. About 90% of the replies checked periodicals. In contrast only 12.5% indicated that students learn anything about patents except to use a secondary source such as *CA*. This is probably the most unfortunate implication of the survey data, since in 1959 over 21% of all abstracts in *CA* covered patents. Even more striking is the low rating accorded governmental bulletins, 3.8%. Manufacturers' technical publications also are less often consulted than are bibliographies, indexes, monographs, etc.

Whatever the preferences of readers may be, we again use this page to urge consideration of the importance of this phase of a student's training. [It is a familiar theme; see for example **35,** 217 (1958).] Modern training not only must meet modern problems, it must anticipate future ones. No more pressing need exists than to know how to handle—or at least approach sensibly—the problem of the rapidly growing printed record of chemical research.

A ChemEd SYMPOSIUM

Chemistry of the Solid State

Introduction

The present surge of interest in crystal chemistry has come about through some recent dramatic events. Most notable has been the invention of the transistor; less in the public notice, but with no less importance to the chemist and teacher seeking an understanding of the behavior of matter, are scores of other new developments in electronics, metallurgy, magnetic materials, and light production which are the immediate result of new ideas about the solid state.

The proper concern of the chemist (besides curiosity) with these matters should be twofold. First, chemists are involved in the purification and fabrication of the materials themselves. In a field of endeavor where "reagent grade" is synonymous with "grossly contaminated," the preparative skill of the chemist and his skill in analysis receive the sharpest challenge. Second, while the theories and methods of the solid state have been applied most intensively by physicists and engineers, there are few problems in chemistry upon which such methods could not be brought to bear with profit. Catalysis, electrochemistry, ceramics, crystallography, radiation damage, corrosion, and coordination chemistry, to name a few, are fields in which an appreciation of modern views of the solid state is prerequisite to reading the current literature and, even more so, to sensible teaching.

A conventionally-trained chemist must be struck immediately by the preoccupation of the solid-state people with defects, impurities, and irregularities in crystals. This should not be surprising in the least; the perfect crystal is viewed as a sort of "solvent" in which the defects are distributed. An unoccupied lattice site has a much more interesting effect upon the properties of a crystal than does an atom in a normal site. Honig (*1*, *2*) has published a good introduction to the role of imperfections in crystals, and Morrison (*3*) treated the effects of defect structures on solid surfaces, as part of a 1957 symposium concerned with solids. Impurities, particularly those of valence differing from the atoms of the host crystal, products of high-energy radiation, and atoms incorporated in excess of normal stoichiometry, all can be considered imperfections having a marked effect on the chemistry and physics of crystals (*4*, *5*, *6*). The interactions between these entities comprise a fascinating chapter in solid-state chemistry, the groundwork of which was laid more than thirty years ago by Wagner and Schottky.

The behavior of electrons in solids is not so readily visualized by one accustomed to dealing with isolated atoms and molecules. When N atoms, each having n electronic energy levels, are brought together to form a crystal, there result Nn levels for the crystal as a whole. These are spread into bands of very closely spaced levels (*7*). Whether, in an electric field, the electrons can gain energy from the field (and by so doing, conduct) depends upon whether higher empty energy levels are readily accessible. Insulators are characterized by an exactly filled valence band, above which lies an energy gap in which no levels exist (analogous to the regions between discrete levels in free atoms). The valence electrons of metals occupy an unfilled band, the conduction band. Semiconductors are (*a*) solids in which the gap between the filled valence band and the conduction band is small enough so that electrons are excited to the conduction band by thermal energy, or (*b*) crystals having levels in the energy gap introduced by imperfections, either chemical or structural, to which or from which electrons can be exited by thermal energy. Note that the removal of an electron from a filled band creates a hole (an empty energy level) which allows electronic conduction in the valence band.

It is clear that the interplay of foreign atoms, vacant lattice sites, electrons and holes all "dissolved" in the otherwise perfect crystal provides a situation in which the principles governing chemical processes can be put into practice with novel and interesting results.

The six symposium papers to be published in THIS JOURNAL treat as many quite distinct aspects of solids. The theme of the symposium was skillfully set and the introductory theory presented by professor J. W. Mitchell, University of Virginia.

Allen B. Scott, *symposium chairman*
Oregon State College, Corvallis

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(4) JOHNSTON, W. D., *ibid.*, **36**, 605 (1959).
(5) TAYLOR, E. H., *ibid.*, **36**, 396 (1959).
(6) BREWER, L., *ibid.*, **38**, 90 (1961).
(7) For a concise treatment of the behavior of electrons in solids see SLATER, J. C., "Quantum Theory of Matter," McGraw-Hill Book Co., Inc., New York, 1951, Chapters 10 and 12.

Howard W. Etzel
U. S. Naval Research Laboratory
Washington, D. C.

Ionic Crystals

Two observations can be made about research on ionic crystals as revealed in the published literature. First, most of the investigations of the physical properties of these materials have been carried out on the alkali halides, and second, since 1925 the investigations have been primarily concerned with the role played by imperfections in determining the properties of crystals. This paper will discuss the latter work.

Because of their simple structure, the alkali halides were the first crystals to yield to detailed calculations of lattice energy. The properties of the ideal lattice have been thoroughly discussed (*1, 2, 3*).

Frenkel, in 1926 (*4*), and Schottky, in 1935 (*5*), developed theories regarding the presence of interstitial and vacancy defects in crystals which were in thermal equilibrium. The idea of a dislocation was developed in 1934 by Taylor (*6*) and Orowan (*7*). Impurities may also be considered defects, since their presence disturbs the periodicity of the lattice. In addition to these imperfections, there are the electrons, holes, and excitons produced by radiation. Combinations of these imperfections with vacancies create another group of defects known as color centers; these have been most intensively investigated in the past 30 years.

Vacancies and Interstitials

Measurements by Tubandt in the early 1930's indicated that the conductivity of alkali halides is ionic. If the lattice is perfect, it is difficult to understand how a field of a few hundred volts per centimeter can be responsible for the observed conductivity. The binding energy of an ion in a normal lattice position is about one electron volt and would require a field of millions of volts per centimeter to dislodge it. Theoretical investigations by Frenkel (*4*), Wagner and Schottky (*8*), Schottky (*5*), Jost (*9*), and later Mott and Littleton (*10*) have shown that if imperfections are assumed to be present in the lattice, the observed conductivity can be explained on this basis. Frenkel proposed that in certain crystal structures a number of ions had been removed from their normal sites and displaced to interstitial positions in the lattice. Conduction can then take place either by motion of the vacancies created when an ion is removed to an interstitial position, by the motion of the interstitial ions, or by both. Schottky (*5*) has proposed that ions may be removed from their normal sites to the surface of the crystal, producing a vacancy at the normal site. The positive and negative ion vacancies created in this manner will be equal in number since the crystals must remain electrically neutral. Conduction, in this case, can occur either by the movement of positive- or negative-ion vacancies or both. Schematic representations of Frenkel and Schottky defects are shown in Figures 1(*a*) and 1(*b*) respectively. Theoretical investigations of Schottky (*5*), Jost and Nehlep (*11*), and Mott and Littleton (*10*) indicate that the Frenkel defects are most probable in the silver halides and Schottky defects most probable in the alkali halides. For the alkali halides

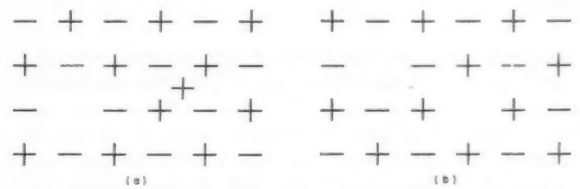

Figure 1. (a) Frenkel defect in the cation sublattice; (b) Schottky defect.

then, Schottky defects predominate and it can be shown that positive ion vacancies are the charge carriers. The conductivity varies with temperature in the following way:

$$\sigma = \sigma_0 e^{-(U + .5W)/kT}$$

where U is the activation energy for a jump, W is the energy to form a pair of vacancies, k is Boltzman's constant, and T the absolute temperature. A typical curve of the dependence of the conductivity upon temperature is shown in Figure 2. Above the knee in the curve both the mobility and the number of charge carriers vary with temperature whereas below the knee the number of charge carriers is fixed by the presence of impurities and only the mobility varies.

Dislocations

The need for invoking the concept of dislocations arose in the early 1930's when investigators concerned with the plastic deformation of solids observed that a slip of several microns occurred on planes separated by about a micron. The strengths of crystals predicted on the basis of a perfect crystal were about one thousand times greater than was observed experimentally. Certainly if the lattice were perfect, a uniform simultaneous gliding of adjacent planes of atoms should occur. Theory and experiment agree when the concept of dislocations is invoked.

Dislocations may be considered as defects associated with the misregistry of two adjacent parts of the lattice.

Presented as part of the Symposium on Chemistry of the Solid State before the Division of Chemical Education at the 138th Meeting of the ACS, New York, September, 1960.

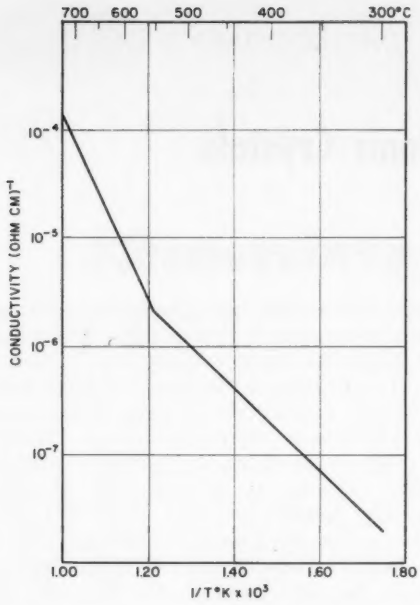

Figure 2. The temperature dependence of the conductivity in sodium chloride.

Basically there are two kinds of dislocations: edge dislocations and screw dislocations. The edge dislocation is shown in Figures 3*a* and 3*b*. Such a dislocation may be thought of as due to an extra plane of atoms extending only part way into the crystal having been produced by the slip of one part of the crystal over another part of the crystal one atomic distance. The line in the interior of the crystal in Figure 3*a* is the edge dislocation. Edge dislocations may not lie entirely in the same line of atoms, but may jump to an adjacent slip plane. The point where such a jump occurs is called a jog. An edge dislocation can move in two ways: it may glide where the movement is in the direction of slip but perpendicular to itself or it may climb where the movement is out of the glide plane. The latter motion is more difficult since atoms must be added or removed from a jog, thus forming vacancies or interstitial atoms in the crystal. Such a motion may be expected to occur at elevated tempera-

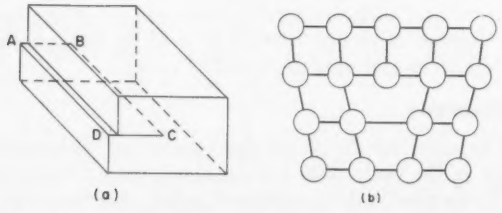

Figure 3. (a) An edge dislocation line *BC* produced by a stress in the plane of *ABCD* and perpendicular to *BC*. (b) Atomic configuration of an edge dislocation.

tures and during annealing processes. The enhanced ionic conductivity observed by Gyulai and Hartly (*12*) following plastic deformation is an example of this mechanism. A screw dislocation is shown in Figure 4 and may be visualized as a helical pattern in the lattice, with no specific slip plane.

Since the crystal is distorted in the neighborhood of a dislocation there are stress fields set up. There is then a tendency for impurities or vacancies to cluster near the dislocation in order to minimize the strain energy. Hence dislocations can act as sinks for vacancies as well as sources.

The origin of dislocations is not well understood. It may be that they arise accidentally during the growth process of the crystal because of the presence of impurities. Mitchell (*13*) has indicated that with extremely pure crystals the dislocation content is so small that cleavage is impossible at room temperature. In contrast to vacancies and interstitials, dislocations are not an equilibrium imperfection. Thermodynamics cannot account for the observed densities of dislocations found in crystals.

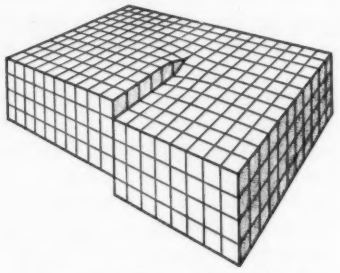

Figure 4. Schematic representation of a screw dislocation.

Impurities

Impurities in single crystals of the alkali halides may be divided into two general categories: Those impurities which are inadvertently present and those impurities which are intentionally added to the melt during the growth process. In the former group are impurities which are present in the charge used for the single crystal growth and those which are introduced if the crystal is grown in air. Certain impurities like lead, silver, and thallium introduce bands in the optical absorption spectra. Crystals containing these ions also luminesce when excited by light in these absorption bands. Divalent positive impurities enhance the ionic conductivity of alkali halides as shown in Figure 5. Many of these same impurities increase the radiation sensitivity of the host crystal. This aspect will be discussed in greater detail in a later section of the paper.

One effect of intentionally added impurities is described by the work of Pick and Weber (*14*). Their work shown in Figure 6 indicates that the density of KCl crystals doped with divalent calcium decreases as one would expect if the calcium ions substituted for the potassium ions and a positive ion vacancy was created for each calcium ion added. The upper line indicates what would be expected if the densities were additive, the bottom line indicates the substitution just described, and the dotted line the experimental data. Since the conductivity is primarily dependent upon the number and the mobility of positive ion vacancies, the introduction of divalent ions into the lattice increases the positive ion vacancy content and hence the ionic conductivity. This is shown in Figure 5, where the conductivity is plotted as a function of the

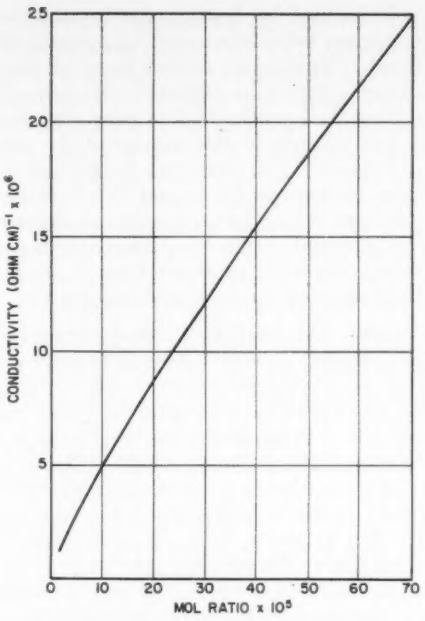

Figure 5. Electrical conductivity at 403°C. of NaCl containing cadmium ions as a function of cadmium ion concentration.

divalent ion concentration. The small amount of curvature in this figure indicates that not all the charge carriers (positive ion vacancies) are free to contribute to the conductivity. A certain fraction are associated with the divalent ions. Recently Rolfe (*15*) and Etzel and Patterson (*16*) have shown that the presence of hydroxyl ions in air-grown alkali halides affects many of the properties of the crystals. After identifying the impurity, crystals were grown with the addition of alkali hydroxide to the melt to observe these effects under controlled conditions. The effect of hydroxyl ions on the sensitivity of alkali halides to ionizing radiation will be discussed in a later section.

Free Electrons and Holes

In the band picture of an insulator the top of the filled band (valence band) and the bottom of the conduction band are separated by several ev. Hence at ordinary temperatures there is no electronic conduction. In metals where the available electrons do

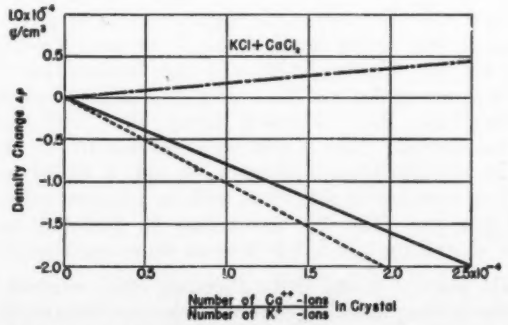

Fig. 6. Change in density of KCl as a function of the addition of $CaCl_2$ (solid line is the experimental data). The upper curve is that change expected if the densities of the two salts were additive. The lower dashed curve represents the expected density change if a calcium ion plus a cation vacancy replaced two potassium ions.

Figure 7. Schematic band picture of an alkali halide showing exciton levels, donor levels, (e.g., *F* centers), and acceptor levels (e.g., *H* centers).

not fill the levels in an allowed band, conduction is possible even at very low temperatures. Intermediate between these two cases are semiconductors which like the insulators have a forbidden energy gap between the valence and conduction bands, but of the order of an electron volt or less. In this case electrons may at finite temperatures be thermally excited to the conduction band. When electrons are excited into the conduction band, holes are left behind in the valence band and they may also contribute to the conductivity. Impurities may contribute to the conductivity by introducing energy levels in the forbidden gap from which or to which electrons may be excited. Those impurities that release electrons to the conduction band are called donors and those that trap electrons excited from the valence band are called acceptors. A pictorial representation of the band scheme in insulators is shown in Figure 7. A transition from the valence

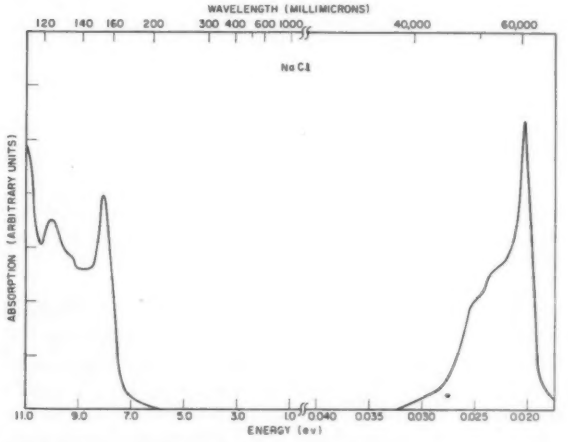

Figure 8. Ultraviolet and infrared absorption spectra of an alkali halide.

band to the conduction band in the alkali halides requires of the order of 6–10 ev. The corresponding optical absorption occurs therefore in the ultraviolet region of the spectrum. The spectrum as shown in Figure 8 has considerable structure. The alkali halides are optically clear in the visible region of the spectrum but absorption again occurs in the infrared due to vibration of the lattice ions.

Excitons

In the case of fundamental band absorption the electron associated with the halide ion is removed from the ion to the conduction band. If however the energy is sufficient only to raise the halide valence electron into an excited state so that it is still bound to its hole, then the entity is called an exciton. The electrically neutral unit so formed is free to travel through the crystal and hence transports energy but no electrical

charge. Experimental measurements indicate that the longest wavelength absorption in the ultraviolet region of Figure 8 is an exciton band since no photoconductivity is observed when light of this wavelength is absorbed.

Color Centers

When the alkali halides are exposed to ionizing radiation, electrons may be stripped from the halide ions. The resulting halogen atom may be thought of as a halide ion plus a positive hole. Not only may the electron be free to wander through the crystal but the hole may move from halide ion to halide ion in the crystal. Most of the electrons so freed are retrapped by the hole and hence returned to their original state. However a certain number of electrons are trapped by other positively charged points in the lattice. A negative ion vacancy represents such a trap for an electron. Dipositive ions are in the same category. In the same manner positively charged holes may be

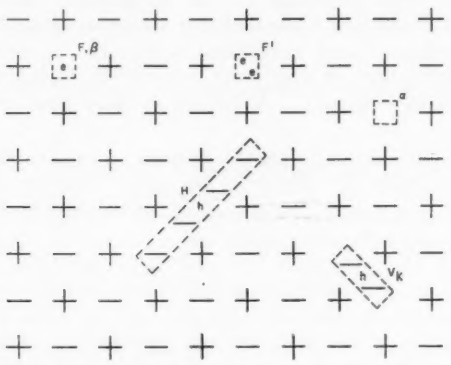

Figure 9. The current models for the F, F', α, β, H, and V_K centers in the alkali halides.

trapped at negatively charged defects. An electron trapped at a negative ion vacancy is called an "*F* center" and gives rise to an optical absorption band usually in the visible region of the spectrum. Centers associated with holes trapped at positive ion vacancies are called "*V* centers" and their absorption bands generally lie in the ultraviolet region of the spectrum. *F* and *V* centers created by ionizing radiation can be removed by heating the crystals to a few hundred degrees Centigrade. At these temperatures the electrons are thermally released from their traps and recombine with the holes. Even at room temperature the bands created by ionizing radiation are not optically stable. Irradiation into the *F* band produces, at the expense of the *F* band, other bands denoted as R_1, R_2, *M*, and *N* bands. The centers responsible for these bands will not be discussed since not enough is presently known about them other than the fact that they are due to electrons trapped at lattice defects. Since the *F* center is analogous to a hydrogen atom it is expected that the *F* center would have a series of excitation levels. Lüty (*17*) has observed four bands on the high energy side of the *F* band which he ascribes to such states.

Color centers which are produced by adding a stoichiometric excess of alkali ions to a crystal are much more stable than those created by radiation. The excess is developed by heating the crystals to a few hundred degrees below their melting point in an alkali metal vapor. New layers of ions form on the crystal surface when halide ions diffuse to the surface. The electron from the deposited alkali atom diffuses to the negative ion vacancy in the interior of the crystal to form an *F* center; *V* centers may be formed in a similar fashion by heating the crystal in a halogen vapor. Hence one can obtain either electron centers or hole centers but not both. The same effect can be produced by injecting electrons or holes from a point probe while the crystal is at an elevated temperature.

The centers just discussed, whether produced by ionizing radiation or by additive coloration, were created at room temperature or above. It is possible to color crystals with ionizing radiation at temperatures as low as 4°K. Much work has been done on coloration at this temperature and at 78°K. The *F* band appears at all temperatures in the range from 4°K to room temperature when a crystal is exposed to high energy radiation. At 4°K only the *F* band and a band of shorter wavelength form. The shorter wavelength band is referred to as the *H* band by Duerig and Markham (*18*), who first observed it. The model originally suggested for the *H* center by Seitz was a hole trapped at a pair of vacancies (one positive and one negative). This center would have a ⟨100⟩ symmetry. The work of Compton and Klick showed that the *H* center must be different from any of the proposed models. They observed dichroism in the *H* center after bleaching with polarized light. According to Compton and Klick the optical dipole moment of the *H* center is parallel to the ⟨110⟩ direction. Subsequent work by Känzig and Woodruff (*19*) established the *H* center as a trapped hole center in which the halide ion with a hole is trapped interstitially and the hole is shared by two halide ions and to a lesser extent with two more halide ions. In effect then the *H* center, shown in Figure 9, is composed of four halide ions occupying three halide sites with a trapped hole, the center lying in a ⟨110⟩ direction in the crystal.

The first electron resonance of a *V* center was reported by Känzig (*20*). This center was produced by subjecting a crystal to X-rays at 78°K and was originally reported by Känzig to be the V_1 center (a hole trapped at a positive ion vacancy). Later work by Delbecq, Smaller, and Yuster (*21*), who combined optical measurements with the resonance measurements, showed that the resonance signal was from another trapped hole center and not the V_1 center. Castner, Känzig, and Woodruff (*22*) were able to show that the center, now called the V_K center, is due to a halogen molecule-ion X_2^-, oriented along the ⟨110⟩ axes of the crystal. The V_K center is formed by the loss of an electron from a halogen ion and a subsequent pulling together of this atom with an adjacent normal halogen ion. The V_K center may be pictured as a hole shared by two halide ions as shown in Figure 9.

The current model of the *F* center, often referred to as the de Boer model, is that of an electron trapped at a negative ion vacancy. An alternative model involving the trapping of an electron at an interstitial alkali ion has been considered an inferior choice mainly because of the calculations of Mott and Littleton (*10*)

Their theoretical argument against the interstitial atom is that nearly 1 ev more energy is required in the alkali halides to form a Frenkel defect than to form a Schottky defect. The most convincing evidence for the de Boer model of the F center comes from spin resonance measurements. A quantitative interpretation of the shape and breadth of the resonance spectrum by Kip, Kittel, Levy, and Portis (*23*) indicated that the electron in the halide ion vacancy interacts not only with the six nearest-neighbor alkali ions but to a lesser degree with the nearest twelve halide ions. By substitution of K^{41} for K^{39} in KCl, a predicted sharing of the resonance line was observed, demonstrating that the broadening does arise from the interaction of the F center electron with the nuclear spins of the neighboring ions. Using an electron spin double resonance technique Feher (*24*) has shown directly the hyperfine interaction of the F center electron with its nearest neighbors.

The other well-known color center for which good experimental evidence exists is the F' center. The F' center is formed by irradiating an F centered crystal with light in the F band at temperatures below 150°K. The F' band is not thermally stable at room temperature. The quantum efficiency measurements of Pick (*25*) indicate that at −100°C two F centers are destroyed for each quantum absorbed. The data are consistent with the model of the F' center being due to two electrons trapped at a halide ion vacancy. Furthermore at the lowest temperatures, light absorption in the F' band destroys one F' center and two F centers are formed.

In the region of the tail of the fundamental band there are two absorption bands due to a perturbed lattice absorption. When an alkali halide is colored with F centers a band designated as the β band is observed on the low energy side of the exciton bands. When the F band is optically bleached the β band decreases and another band designated as the α band appears at a still lower energy. These bands were first observed by Delbecq, Pringsheim, and Yuster (*26*). Their interpretation of these bands is as follows: The β center is presumed due to the perturbation by an F center of the exciton absorption. The α band which appears when the F band (and therefore the β band) bleaches is presumed due to a stronger perturbation of the exciton absorption by an anion vacancy. The α and β bands have only been observed at temperatures below 100°K.

It appears then, that at the present time, one has rather well established models for the F, F', α, β, H, and V_K bands as shown in Figure 9. The state of our understanding of the M, R_1, R_2, N, O, V_1, V_2, V_3, V_4, etc. bands is incomplete.

Generation of Defects in the Alkali Halides

Of the many problems that are currently being investigated in the alkali halides, one which has received considerable attention and is not yet completely solved is the problem of the generation of defects, and hence color centers, by high energy radiation. High energy radiation shall be defined here as X-rays, gamma rays, and Mev electrons.

The most recent work on the generation of color centers at 4°K by Rabin and Klick (*27*) will be discussed first. All the earlier work was done at higher

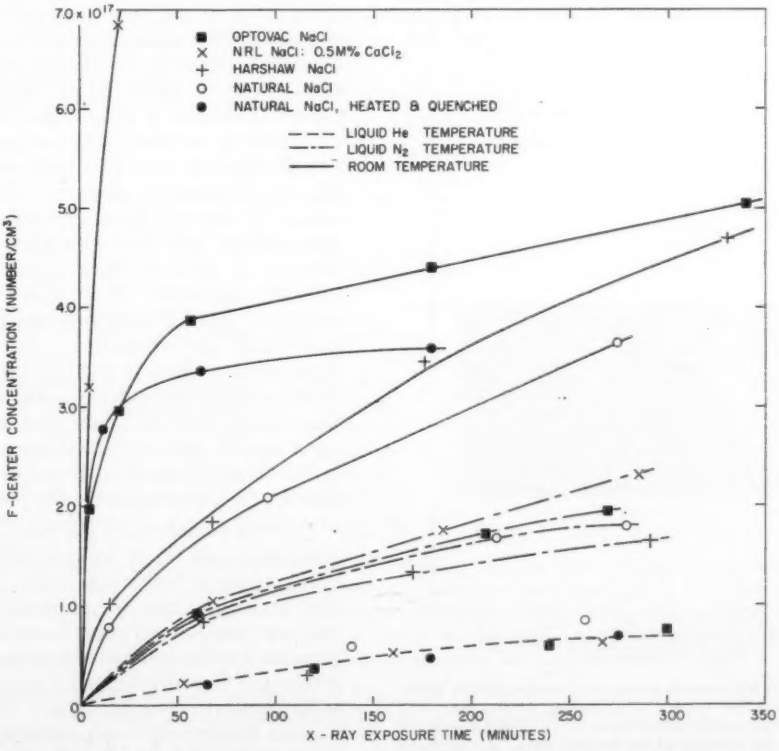

Figure 10. *F* band growth in various NaCl crystals irradiated with X-rays at room, liquid nitrogen, and liquid helium temperatures.

temperatures where the picture is still not clear. Rabin and Klick found that about 1.3×10^3 ev was required to form an *F* center in KCl at 4°K. If the crystals were optically bleached and reirradiated at the same temperature, it was then found that only 28 ev were required to form an *F* center. This suggested that the large expenditure of energy in the first irradiation was required to generate isolated vacancies and fill them with electrons; and that the second irradiation colored the crystal efficiently because the optical bleach did not remove the radiation-produced vacancies. It was only necessary to generate electrons to produce *F* centers. The number of *F* centers created at 4°K was independent of crystal purity and dislocation content; this suggested that these entities are not involved in the production of vacancies. This is shown in Figure 10 where crystals of different purity were irradiated. Since the *F* and *H* centers are formed simultaneously at 4°K, the process then does not involve the alkali ion sub-lattice. Previously it had been assumed (*28*) that positive and negative ion vacancy pairs were formed by the climb of dislocation lines. Then, presumably, the pairs diffused away from the dislocation and were broken up when they trapped an electron. No source of interstitial halogen atoms is accounted for by this mechanism. It is to be recalled that Duerig and Markham (*18*) have shown that *H* centers are present in crystals irradiated at 4°K.

Figure 11 shows the dependence of the efficiency of producing *F* centers at 4°K upon the halide ion spacing by ionizing radiation in different alkali halides. It will be noted that the efficiency is high when the space

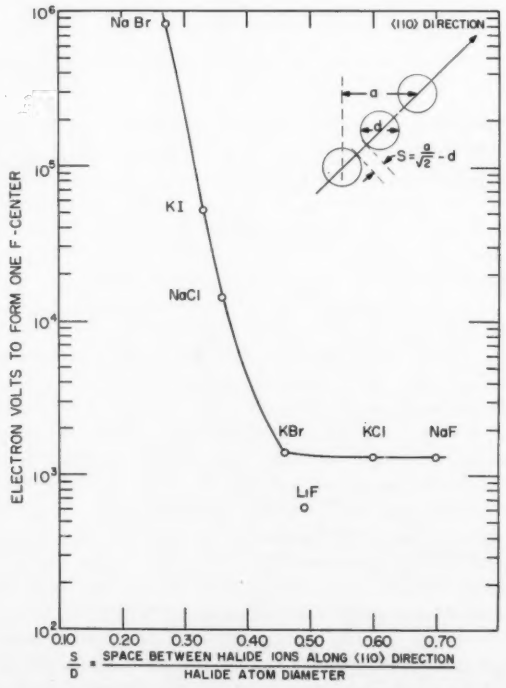

Fig. 11. Total X-ray energy required to form an *F* center at liquid helium temperature for various alkali halides as a function of the ratio *S/D*, where *S* is the space between adjacent halides in the ⟨110⟩ direction of the normal lattice and *D* is the diameter of the halogen atom. *S* is given by $[(a/\sqrt{2}) - d]$ where *a* is the lattice constant and *d* is the halide ion diameter.

between two adjacent halide ions in the ⟨110⟩ direction is greater than half the atomic diameter of the halogen atom. Hence a halogen atom may be fit interstitially by moving each of two halogen ions a distance of $S/_2$ further apart. According to Rabin and Klick the efficiency with which anion vacancies and hence *F* centers can be formed at 4°K is determined by the ease with which *H* centers are formed.

The mechanism by which the radiation energy is absorbed is not yet well established. Irradiation into the fundamental band with exciton wave-length light has not produced *F* and *H* centers at 4°K (*29*). So it would appear that the energy released to the lattice upon the decay of an exciton is not sufficient. It is possible that the centers may be formed by a single ionization of a halide ion. The ionization may cause a relaxation of the lattice in the vicinity of the so-formed halogen atom; since the nearest neighbors are set in motion, the atom which is being uncharged may diffuse to an interstitial postion to form an *H* center while the electron is trapped by the anion vacancy to form an *F* center. Another possibility first suggested by Varley (*30*) is that a double ionization process may be responsible for producing color centers at 4°K. In this situation the halogen ion becomes positively charged by the loss of two electrons and is thereby ejected from the normal lattice site into an interstitial position where it retraps one electron to form an *H* center. The other electron goes to an anion vacancy to form an *F* center. Dexter (*31*) has pointed out that the very high electron affinity of the positive halogen ion assures that this ion will quickly trap an electron, probably from a neighboring halide ion; thus the electrostatic forces tending to displace the ion will be nullified. Klick (*32*) has pointed out that the energy released by the transfer of an electron from a neighboring halide ion may be utilized in producing an interstitial-vacancy pair. After the transfer occurs, the halogen molecule is small (the two halogen atoms are attracted by electron exchange forces) and the molecule can fit into the site occupied by one ion leaving an adjacent halide-ion vacancy. The jump of a neighboring ion into the vacancy results in the separation of the vacancy and the molecule. The trapping of an electron by each of these defects generates *F* and *H* centers. Evidence from spin resonance (*19*) and polarized light (*33*) measurements indicates that there is virtually no interaction between *F* and *H* centers when they are both in their ground states; thus the interstitial must be located several lattice sites away from the vacancy. It is likely that at such low temperatures as 4°K the ejection of an atom may be required rather than diffusion. It is not possible at this time to decide which mechanism is the proper one.

At room temperature the data indicate that the rate of formation of the *F* band is strongly dependent upon the presence of impurities (*34*). In Figure 12 one sees that the initial rate of coloration is influenced by the presence of hydroxyl ions; however, for very high doses of radiation, there is an indication that the energy absorbed per *F* center formed is about the same regardless of the impurity concentration. This suggests that even at room temperature the possibility of forming vacancies and interstitials must be considered. The mechanism for the production of defects at room temperature will

undoubtedly be better understood when expansion measurements coupled with precise lattice parameter measurements are carried out on single crystals free of impurities.

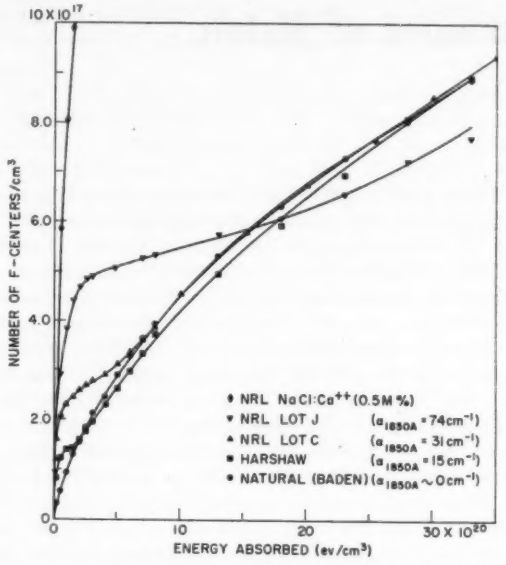

Figure 12. Growth of the number of *F* centers produced in NaCl at room temperature by X-ray radiation as a function of the energy absorbed. The hydroxyl ion content of these crystals is proportional to α_{1850A}.

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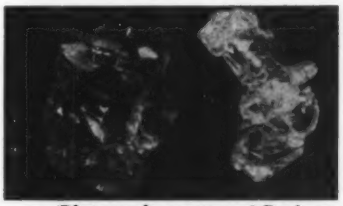
The cover



Photograph, courtesy of Professor Walter J. Moore, Indiana University.

Unfortunately, the cover reproduction does not do justice to the striking color contrast in the photographs of two crystals of zinc sulfide. The crystal on the left is a brilliant red-orange, that on the right is the familiar clear white. These crystals were grown in the laboratories of the American Zinc Company of Illinois by reaction of zinc vapor with oxygen.

Spectrographic analyses show that neither the red-orange nor the white crystals contain more than a few parts per million of metallic impurities. However, the red-orange crystals contain about 0.03% zinc in excess over the stoichiometric quantity for ZnO. The red-orange color is bleached on heating the crystals in oxygen, but can be restored by heating in zinc vapor. It is believed that most of the excess zinc occupies interstitial sites in the zinc oxide crystal structure.

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Diffusion in Solids and the Gaseous Corrosion of Metals

Our subject is concerned with the properties in the solid state of metallic oxides and sulfides. The story begins with one of the most famous controversies in the history of chemistry. In 1799, Claude Louis Berthollet (Fig. 1) joined Napoleon's expedition to Egypt as one of the scientific advisors. While there he studied the deposits of sodium carbonate along the shores of the salt lakes and became interested in the chemical reactions that could lead to such deposits. He concluded that the important reaction was

$$NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

Under ordinary laboratory conditions this reaction proceeds from right to left with the precipitation of $CaCO_3$. However, Berthollet suggested that the large excess of NaCl in the evaporating brines might displace the equilibrium to the right. This idea was one of the first statements that concentration could affect the position of a chemical equilibrium.

Figure 1. Claude Louis Berthollet, 1748–1822. (Photograph courtesy of Professor J. Bénard, University of Paris.)

Berthollet expanded this idea in his famous book "Essai de Statique Chimique" published in 1803. He failed to distinguish clearly between the composition of individual compounds entering into the reaction and the composition of the reaction mixture. A key example was zinc oxide; he prepared it in various ways, and found widely varying ratios of zinc to oxygen.

Berthollet was an imaginative chemical theorist but he was not a first class analyst. On the other hand, Joseph Proust, perhaps the finest analyst of his day, was then working in Spain in a splendidly equipped laboratory (all the utensils were made of platinum). Whenever Berthollet reported a compound departing from normal stoichiometry, Proust carefully repeated the work and showed that in fact the proportions of the elements were perfectly normal. Thus Proust won an undisputed victory in the controversy and the Law of Definite Proportions became firmly established. As a result, John Dalton was able to rely on this law when he formulated his atomic theory in 1808.

It is therefore ironical to relate that through his mistakes Berthollet won an immortal niche in the chemical nomenclature. His imaginative approach to chemical stoichiometry was eventually proved to be correct. There are many compounds, especially among crystalline inorganic solids such as metallic oxides and sulfides, which do not follow the Law of Definite Proportions. We now call these compounds *berthollides* to distinguish them from the *daltonides* which have a definite simple stoichiometric composition. Solid state chemistry to a considerable extent is the chemistry of the berthollides.

Zinc oxide crystals can be prepared with colors from pure white to deep red. The white crystals have a Zn/O ratio of almost exactly unity. The red crystals contain about 300 ppm excess zinc. We might note that this excess of zinc is about 100 times lower than that cited by Berthollet, but nevertheless we must admit that zinc oxide is a typical berthollide and many of its most interesting properties depend on this departure from stoichiometry.

Point Defects and Diffusion in Solids

We shall now make a considerable jump in the historical development of the subject and come to the question of the structure of these nonstoichiometric or berthollide solids. This question arose, it would seem, from an interest in the movements of atoms within solids. In 1896 a striking early observation was made by Roberts-Austen in his paper on diffusion of gold in lead. He showed that at 300°C gold would diffuse in lead faster than sodium chloride would diffuse through water at 15°C. As the development of X-ray crystallography revealed more about the ordered structure of solids, it became more and more difficult

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to understand how atoms in metals, or ions in alkali halides, could diffuse so readily if, in fact, the elementary diffusion reaction demanded that one atom must change place with a neighbor in a rigid array in the solid. On the experimental side the application of radioactive tracers to diffusion studies, originally made by von Hevesy, led to an outpouring of experimental data.

New mechanisms for diffusion were finally suggested by the Russian, Frenkel, in 1926, and by the German, Schottky, in 1930. These were the first exact models for what are now called *point-defects* in crystals. The Frenkel defect is shown in Figure 1(*a*) of the paper by H. Etzel in this symposium (see page 225), as originally proposed for silver chloride. It consists of an Ag^+ ion that has left its lattice site and moved to an interstitial position. The Frenkel defect consists of the vacancy plus the interstitial. The Schottky defect is shown in Figure 1(*b*) of the paper by Etzel, as in the case of sodium chloride. It consists of a pair of vacancies of opposite sign. These defects are called *intrinsic defects*. They do not alter the exact stoichiometry of the crystal, but they provide a facile mechanism by which atoms can move within the crystal. It is much easier for an atom to move from an occupied site into a vacancy than it would be for two atoms in occupied sites to change places directly.

We can calculate the concentration of such defects from simple statistical considerations. It costs an energy E to make a defect but we gain entropy S due to the disorder associated with the entropy of mixing of the defects with the normal lattice sites. If n imperfections are distributed among the total of N crystal sites, the entropy of mixing is

$$S = k \ln N!/(N - n)!\, n!$$

If E is the increase in energy per defect and if we neglect contributions to the energy caused by changes in vibration frequencies in the neighborhood of the defect, we can write for the change in the Helmholtz free energy

$$\Delta A = \Delta E - T\Delta S$$

$$A = nE - kT \ln N!/(N - n)!\, n!$$

At equilibrium,

$$\partial A/\partial n = 0$$

Applying the Stirling formula, ($\ln X! = X \ln X - X$), we find,

$$\ln [n/(N - n)] = -E/kT$$

And thus if $n << N$,

$$n = Ne^{-E/kT}$$

As an example, if E is about 1 ev and T is 1000°K

$$n/N \sim 10^{-5}$$

For a pair of vacancies the expression for the number of ways forming the defect is squared and we get finally, for the Schottky defects,

$$n = Ne^{-E/2kT}$$

For Frenkel defects,

$$n = (NN')^{1/2}e^{-E/2kT}$$

where N' is the number of interstitial sites available.

An important experimental proof that defects are in fact responsible for diffusion in solids was provided in 1946 by the experiment of Smigelskas and Kirkendall. A similar experiment had previously been done on diffusion in iron oxides by Pfeil in 1929. In the classical mechanism of diffusion, two particles exchange sites by a sort of rotatory process. In a binary system, therefore, the diffusion of component A is always coupled with an inverse diffusion of component B. There is in fact only one diffusion coefficient, the interdiffusion coefficient D_{AB}. On the other hand, if diffusion proceeds by motion of an atom into a vacancy or by some other defect mechanism, it is possible for one component to diffuse at a different rate from the second component. Of course, this difference in diffusive flow will need to be compensated by some over-all mass motion in the specimen.

The experiment of Kirkendall is shown in Figure 2. The original location of the interface between blocks of copper and of brass was marked by imbedding fine molybdenum wires. After the diffusion anneal it was found that the markers had moved inward toward the brass. The motion of the inert markers clearly indicated that the zinc was diffusing out of the brass more rapidly than the copper was diffusing into it.

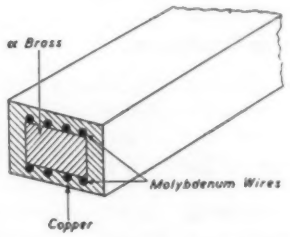

Figure 2. The experiment of Smigelskas and Kirkendall.

Nonstoichiometric Defects

In 1930, Wagner and Schottky applied the models of defect structures to nonstoichiometric compounds of the berthollide type. We can take two compounds as typical, zinc oxide and nickel oxide.

The structure of ZnO is shown in Figure 3. When heated in a reducing atmosphere or in zinc vapor, it acquires a stoichiometric excess of zinc, of the order of 0.03%. We do not know exactly where this zinc is accommodated, but it is commonly assumed that it

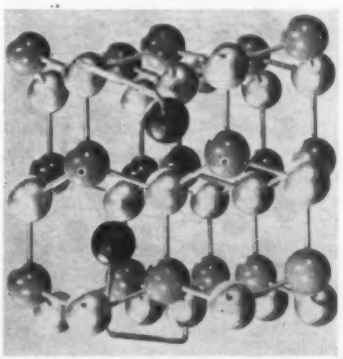

Figure 3. Structure of zinc oxide showing excess zinc at tetrahedral and octahedral interstitial sites.

enters interstitial positions. Two such interstitial sites in zinc oxide occupied by excess zinc atoms are shown. In one, the excess zinc atom is surrounded octahedrally by six oxygen atoms. In the other it is surrounded tetrahedrally by four oxygen atoms. We cannot say which of these sites will be energetically preferred, but both of them seem to be sites of relatively low energy in the crystal.

The case of nickel oxide is typical of the departure from stoichiometry in which the structure contains an excess of oxygen. This excess is believed to enter mainly as vacancies in the cation sites, according to an equation which can be written

$$\tfrac{1}{2}\,O_2 + 2\,Ni^{+2} \rightarrow O^{-2} + 2\,Ni^{+3} + V_{Ni}{}^{+2}$$

For each vacant Ni^{+2} site, two Ni^{+3} ions are formed. In this way the over-all neutrality of charge is preserved.

We can now begin to see why the solid state chemistry of these compounds may be complicated. At moderately elevated temperature both intrinsic defects and nonstoichiometric defects can occur in the same crystal. Also we must consider the possibility that several kinds of nonstoichiometric defect can occur at the same time. For example, the excess zinc in zinc oxide may be partially associated with interstitial zinc and partly with vacancies at the oxygen sites.

The Interdiffusion Coefficient

If both the diffusion coefficients can be measured by tracers in a binary system, we can calculate the interdiffusion coefficient from the individual partial coefficients. An excellent analysis of this problem has recently been given by Brebrick (*1*). Consider a binary solid in which the departure from stoichiometry is Δ (the difference in cation and anion concentrations, $N_c - N_A$). Then the interdiffusion coefficient D_Δ measures the flow of the deviation from stoichiometry. For example, if we place copper(I) oxide previously annealed in vacuum into an atmosphere of oxygen, the crystal will take up extra oxygen. The rate of this uptake is governed by the interdiffusion coefficient D_Δ, which is related as follows to the individual tracer diffusion coefficients $D_A{}^*$ and $D_C{}^*$ for A and C:

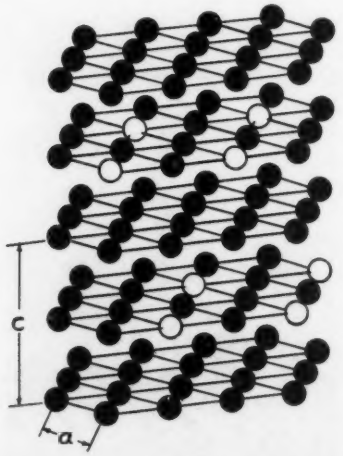

Figure 4. The structure of Fe_7S_8, showing layers of iron atoms only. The white circles indicate vacant iron sites. (After Condit and Birchenall (*6*).)

$$D_\Delta = \frac{N}{kT}(D_A{}^* + D_C{}^*)\frac{d\,\mu_m}{d\Delta} = N(D_A{}^* + D_C{}^*)\frac{d\,\ln a_m}{d\Delta}$$

where N is the number per cc of either cation or anion sites, μ_m is the chemical potential, and a_m the activity of the metallic component. For vacancy defects, $N(d\,\ln a_m/d\Delta)$ is of the order of the reciprocal of V_C the total vacancy fraction, i.e., 10^2 to 10^6. Therefore D_Δ can exceed D_A by about this factor.

In case the nonstoichiometric vacancies greatly exceed the Schottky vacancies the relation reduces to

$$D_\Delta = \frac{2\,D_C{}^*N}{V_C}$$

At 1000°C and $P_{O_2} = 10$ mm, $N/V_C \sim 10^3$. Thus the interdiffusion coefficient is about 2000 times the diffusion coefficient of Cu^+ ions.

Recent Results of Defect Structure Studies

The models suggested for the point imperfections in crystals always seemed reasonable enough, but we could never be sure that we had an unequivocal description of the defect structure. The evidence was usually indirect, based on interpretation of diffusion coefficients, conductivities, densities, and lattice parameters. In the case of the alkali halides, the study of the various optical centers by means of electron paramagnetic resonance and nuclear magnetic resonance often revealed unexpected structures, which required considerable revisions of the earlier simple models. So far only a few such studies have been made with oxides and the results as yet are in a stage of preliminary analysis.

An important new experimental approach has been the use of neutron diffraction. Roth (*2*) has studied the defect structures of iron(II) and nickel(II) oxides by this method. His results indicate that not all the defects caused by excess oxygen are cation vacancies. In FeO systems with Fe/O ratios of 0.945 and 0.926, about 88% of the cation sites were occupied and there was one interstitial iron atom for every two vacancies.

Theoretical calculations indicate that the simple interstitial atom is not likely to occur in a close packed structure. Instead the energy seems to favor a defect called a *split interstitial*. Consider an atom in a face-centered position. If we introduce next to it an interstitial, the face-centered atom can move away, thus forming a pair of atoms with the center of mass at the face center.

In some cases, the vacancies or interstitials may form an ordered *superlattice*. The structure of Fe_7S_8 below the Néel temperature[1] of 320°C is shown in Figure 4 as determined by Bertant (*3*).

Measurement of Diffusion Coefficients

The differential equation governing diffusion in one dimension is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

where c is the concentration of the diffusing species, t is the time, and x is the distance. In case the diffusion

[1] Antiferromagnetic substances display a maximum in the susceptibility versus temperature curve at the Néel temperature T_c. Below this temperature the spins lock in with antiparallel orientations.

coefficient D is a constant, independent of x, the equation becomes

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

There are many useful solutions of this equation depending upon the particular initial and boundary conditions of the problem. One of the methods most commonly used to measure D is to prepare a slab of the solid substance, coat it with a thin layer containing the radioactive tracer which we wish to follow, and then submit the specimen to an anneal for a measured time t at a fixed temperature T. For example, to measure the diffusion of silver in silver sulfide, we coated the surface of the specimen with a thin layer of Ag_2S containing the tracer ^{110}Ag. The diffusing species, in this case, follows a simple Gaussian distribution,

$$c/c_0 = (\pi Dt)^{-1/2} e^{-x^2/4Dt}$$

where c/c_0 is the fraction of the original activity per unit thickness (e.g., 1 μ) at a depth x. The specimen is sliced or ground away and the c/c_0 is measured experimentally as a function of x.

If we take the logarithm of both sides of the equation, we find

$$\ln c/c_0 = -1/2 \ln (\pi Dt) - x^2/4Dt$$

Thus if we plot ln (c/c_0) against x^2, this solution predicts a straight line whose slope is $-(4Dt)^{-1}$. An example from the work with Ag_2S is shown in Figure 5. The slope yields a value $D = 1.23 \times 10^{-5}$ cm^2 sec^{-1} at 283°C. This is an extraordinarily high D. It is about equal to the D that we calculate for silver atoms in a gas at the same density.

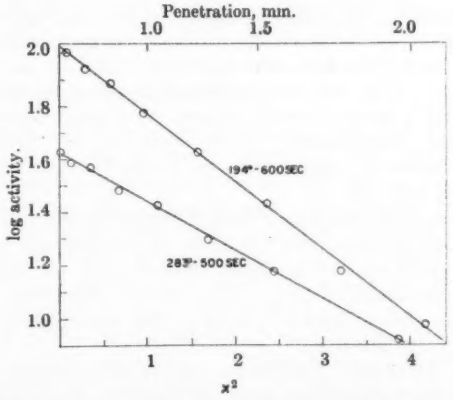

Figure 5. A typical "diffusion profile" for the case of diffusion of ^{110}Ag into cubic Ag_2S.

One other method will be mentioned since it is widely useful, especially for diffusing species for which we do not have a suitable radioactive isotope. A sample of the solid, which may be either a single piece of regular shape or a collection of pieces having the same size and shape, is exposed to gas or solution containing the tracer. An example is our work with the diffusion of oxygen in oxides (*4*). In the case of copper(I) oxides, strips of polycrystalline Cu_2O were exposed to oxygen enriched in the stable isotope ^{18}O. The volume of the gas is fixed. As the ^{18}O diffuses into the Cu_2O, there is an exchange between the oxygen atoms in the gas and those in the solid. The concentration of ^{18}O in the gas gradually decreases. An example of such an exchange run is shown in Figure 6.

The appropriate solution to the diffusion equation is

$$\frac{M_t}{M_\infty} = 1 - \sum_{m=1}^{\infty} \frac{2\alpha(1+\alpha)}{1 + \alpha q_m + \alpha^2 q_m^2} \exp(-Dq_m^2 t/x^2)$$

This gives the total amount M_t of tracer in the solid at time t. The parameter $\alpha = n_g/n_s$, where the n's are the number of moles of oxygen in the gas and in the solid. The q_m's are the nonzero positive roots of tan $q + \alpha q = 0$. By straightforward computational methods, we can evaluate D from the change in isotope concentration in the gas as measured with a mass spectrometer.

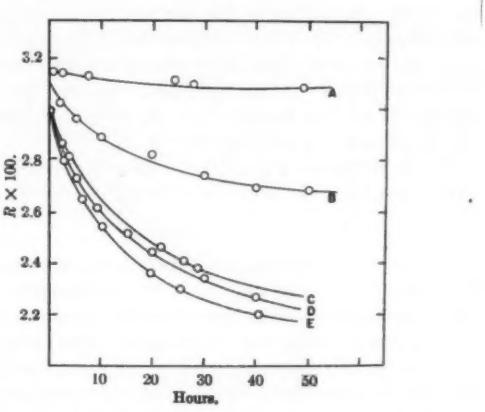

Figure 6. The exchange of ^{18}O in O_2 with ^{16}O in crystals of Cu_2O. *A*, background of mullite tube; *B*, *C*, *D*, and *E*, 970–1100°C. *R* is the ratio $^{18}O\ ^{16}O/^{16}O_2$.

One difficulty with the study of oxygen diffusion by this method is that most high temperature ceramics are made of oxides, so that there is a possibility of exchange between the gas and the walls of the container. We used platinum tubes to eliminate this difficulty, but they begin to fail at about 1400°C. In the experiments of Kingery (*5*), an internal heater was used so that only the oxide crystals were heated while the ceramic walls of the container were cooled.

Some Diffusion Coefficients in Oxides and Sulfides

It is convenient to tabulate diffusion coefficients in terms of the formulation of the transition state theory. Wynne-Jones and Eyring originally applied this to the diffusion problem. They obtained for the diffusion coefficient the expression

$$D = kT/h\ a^2 \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$$

where k and h are the Boltzmann and Planck constants, a is the jump distance in an elementary diffusion step, and $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are the entropy and heat of activation. Some of the available data are collected in Table 1.

Some cases in which the diffusion of both constituents of a solid binary compound have been measured are shown in the table. In these cases the metal diffuses more rapidly than the oxygen or sulfur. This is certainly not an invariable rule. It just happens that we do not yet have good data for the opposite situation.

Table 1. Diffusion Coefficients Measured by Indiana Solid State Group

System	Temperature range, °C	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ cal/deg mole
Cu-Cu_2O	800–1050	34.0	1.0
O-Cu_2O	1000–1130	38.0	− 5.0
Zn-ZnO	1000–1200	45.0	−10.0
O-ZnO	1100–1400	162.0	59.0
Ni-NiO	1000–1400	43.0	− 8.0
O-NiO	1100–1500	51.0	−17.5
Mg-MgO	1400–1600	75.5	2.0
Ag-Ag_2S (α)	180– 400	3.2	− 0.7
Ag-Ag_2S (β)	100– 175	9.5	0.1

In oxides such as TiO_2, UO_2, ThO_2, it is likely that the oxygen diffuses more rapidly than the metal.

We must admit that in none of the systems cited in the table, do we know for certain the mechanism for the diffusion. For the oxides of nickel, copper, cobalt, and other oxides containing excess oxygen, the almost universal belief is that diffusion occurs by way of vacancies at the metal sites. Conclusive proof that this is so is not yet available.

When diffusion occurs by a defect mechanism, we can in certain cases formulate the diffusion coefficient as

$$D = fD_iX_i$$

where D_i is the diffusion coefficient for the defect and X_i is the fraction of defects. We saw before how this was a special case of equations for D_Δ given by Wagner and Brebrick. The f is a *correlation factor*, which arises because individual jumps of a diffusing tracer atom are not completely independent. For example, if a tracer atom jumps into a vacancy, the most likely next jump is right back into the vacancy it has left behind it.

It follows (from the fact that the diffusion coefficient is the product of a defect concentration and a defect mobility) that the activation entropy and energy for diffusion via defects are also composite quantities. They may be written as follows:

$$\Delta S^{\ddagger} = \Delta S^{\circ} + \Delta S_i^{\ddagger}$$

$$\Delta H^{\ddagger} = \Delta H^{\circ} + \Delta H_i^{\ddagger}$$

Here ΔH° and ΔS° are purely thermodynamic quantities, the heat and entropy of formation of defects. $\Delta H_i^{\ddagger}$ and $\Delta S_i^{\ddagger}$ are kinetic quantities, the heat and entropy of activation for the mobility of a defect.

The three important mechanisms which need to be considered in oxides and sulfides are diffusion via vacancies and two different interstitial mechanisms. The direct interstitial mechanism consists of a jump of the tracer atom from one interstitial site to the next with occasionally an exchange between the interstitial atom and an atom in a normal lattice site. The indirect interstitial mechanism, also called the *interstitialcy* mechanism, consists of a migration in which an interstitial atom displaces a normal atom, pushing it into another interstitial site. We might call this a "bimolecular mechanism" whereas the ordinary interstitial mechanism is more like a "unimolecular mechanism."

In ordinary diffusion in the solid state we expect the activation entropy $\Delta S^{\ddagger}$ to be close to zero. None of the diffusion mechanisms that we have mentioned would lead to an appreciable $\Delta S^{\ddagger}$ for the defect mobility. The small negative $\Delta S^{\ddagger}$ sometimes observed for cation diffusion by the vacancy mechanism is believed to be due to the loss in entropy when gaseous oxygen dissolves in a solid oxide to produce cation vacancies. What are we to think of an enormous positive entropy such as that reported for diffusion of oxygen in ZnO? This is not an isolated instance. Condit and Birchenall (*6*) have reported $\Delta H^{\ddagger} = 240$ kcal, $\Delta S^{\ddagger} \approx 150$ cal deg^{-1} mole^{-1}, for diffusion of sulfur in FeS. Similar enormous values of both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found by Reddington (*7*) for diffusion of barium in BaO. All these studies were done with single crystals. It is likely that some of the following factors are involved:

(*a*) Diffusion along dislocations.

(*b*) Diffusion steps with a long mean free path.

(*c*) Diffusion steps that create an extended region of disorder, a sort of cooperative melting over 40 or 50 atoms in the crystal.

Determination of Correlation Factors

We can determine the correlation factor f in crystals in which the diffusing particle is an ion, if we can also measure the partial ionic conductivity in the crystal. Such a determination demands an unusually careful measurement of the radioactive diffusion coefficient D^* and the partial ionic conductivity σ_i. These are related by the equation of Nernst and Einstein,

$$D^* = fkT\sigma/q^2n$$

where q is the charge of the diffusing species and n is the concentration of the ionic carriers. Notice that when we measure σ, the current carriers are indistinguishable from the particles of the same species in the crystal structure. On the other hand, when we measure D^*, the diffusing particles are distinguished from most of the particles of the same species in the structure by the fact that they differ slightly in mass number. It is this distinguishability that leads to a correlation factor f, which differs from unity for some diffusion mechanisms. Note that if the diffusing species does not bear the charge q, the Nernst-Einstein relation will fail.

It may be mentioned that diffusion coefficients determined by resonance methods, or by methods based on internal friction or dielectric loss, will not include the correlation factor. We could therefore also compare D's obtained in such a way with radioactive D's to calculate the f.

The computed correlation factors for different diffusion mechanisms are given in Table 2. It is evident that careful measurements of f will allow us to distinguish between mechanisms in a sensitive way, but it must be admitted that the experimental accuracy required has seldom been achieved in practice. Nevertheless this is the line which is most promising for further work.

One successful application of the correlation factor was in the case of silver bromide. Measurements of D_{Ag^+} and of σ_{Ag^+} by Miller and Maurer (*8*), and by Friauf (*9*), yielded a value of $f = 0.40$, in good agreement with that expected for the *interstitialcy* mechanism. When the crystals were doped with Cd^{+2} ions to introduce vacancies at Ag^+ sites, the f became that of the vacancy mechanism.

Table 2. Computed Correlation Factors for Defect Mechanisms of Diffusion

Mechanism	f—factor
Vacancy, diamond	0.50
Vacancy, f. c. c.	0.78
Vacancy, b. c. c.	0.72
Interstitial	1.00
Interstitialcy	0.33
Ag^+ in cubic Ag_2S	0.50

Another recent example is found in the comparison of the D_{Ag^+} for silver in cubic silver sulfide measured by Allen in our laboratory (*10*) and the σ_{Ag^+} measured by Rickert at Göttingen (*11*). The arrangement used to measure σ is shown in Figure 7. The results yield $f = 0.33$, which is somewhat lower than the $f = 0.50$ predicted for the Ag_2S structure.

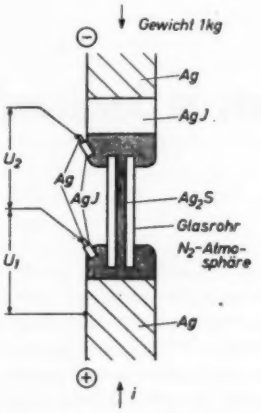

Figure 7. The experiment of Rickert for measurement of σ_{Ag^+} in Ag_2S. AgI conducts only via Ag^+ ions, so that the layer of AgI limits the carriers of current in Ag_2S also to Ag^+ ions.

Theory of Corrosion Reactions

If an attacking reagent forms a coherent layer of product on the surface of a metal, the subsequent reaction will often depend on the diffusion of reactants through the solid product layer. The theory for this kind of diffusion-controlled reaction was worked out in 1933 by Carl Wagner (*12*). Several excellent experimental checks have given us confidence that the Wagner formulation is essentially correct.

Let us consider a simplified case in which only the metal atoms are mobile. This case would apply well in practice to the oxidation of nickel and zinc, the oxidation of copper to copper(I) oxide, and the sulfidation of silver. To take a special example we shall consider the sulfidation of silver at about 177°C to form Ag_2S.

The parabolic rate constant is defined as k_0 in

$$dy/dt = k_0/y$$

where y is the thickness of the sulfide layer. The units of k_0 are usually $cm^2\ sec^{-1}$.

Wagner uses a rational rate constant, k_r, in equivalents $cm^{-1}\ sec^{-1}$. Thus

$$k_r = c_{Ag^+} k_0$$

where c_{Ag^+} is the concentration of silver in the Ag_2S layer, in equivalents per cm^3.

The case of silver sulfide is particularly suitable for a good test of the theory since the diffusion of Ag in Ag_2S is not affected appreciably by differences in stoichiometry. Thus D_{Ag} and σ_{Ag^+} can be taken as constants across the growing sulfide layer. For this case, integration of the equation of Brebrick yields,

$$k_r = \sigma_{Ag^+} \frac{\mu^\circ_{Ag} - \mu^*_{Ag}}{zF^2} = c_{Ag^+} \frac{D_{Ag}^*}{f} \frac{\mu^\circ_{Ag} - \mu^*_{Ag}}{RT}$$

Here μ°_{Ag} is the chemical potential of Ag in Ag_2S in equilibrium with Ag, and μ^*_{Ag} is the chemical potential of Ag in Ag_2S in equilibrium with sulfur. The difference $\mu^\circ_{Ag} - \mu^*_{Ag}$ is simply the affinity of the sulfidation reaction. Note that if the radioactive diffusion coefficient is used to calculate the parabolic rate constant, the appropriate correlation factor must be included.

Recently Rickert in Wagner's laboratory in Göttingen has made some accurate new measurements of k_r and σ_{Ag^+} for the Ag_2S system. His experimental arrangement is shown in Figure 8. By the clever device of imposing a weight on the system as shown, he kept the silver sulfide and the underlying silver always in tight contact. Thus as silver diffused outward through the silver sulfide, the vacancies and void spaces that were left behind at the silver sulfide-silver interface were kept filled by the inward motion of the silver-sulfide rod. By means of a Ag/AgI electrode he also made a continuous measurement of the potential difference at the interface. In the early stages of the reaction there was an appreciable potential difference here, so that the equilibrium criterion was not fulfilled. As the silver sulfide layer became thicker, however, the potential difference across the Ag/Ag_2S interface dropped to virtually zero, and under these conditions it was safe to apply the Wagner formulation for the rate constant. The measured rational rate

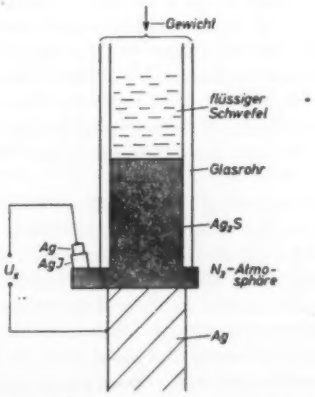

Figure 8. The experiment of Rickert to measure the rate of growth of Ag_2S on Ag while testing experimentally for the existence of equilibrium conditions at the interfaces.

constant at 400°C was $k_r = 14.4 \times 10^{-6}$ equivalent $cm^{-1}\ sec^{-1}$. Rickert also measured the partial ionic conductivity of Ag^+ ions in silver sulfide and computed from it a rate constant of $k_r = 15.0 \times 10^{-6}$ equivalent $cm^{-1}\ sec^{-1}$. This is one of the best proofs of the correctness of the Wagner formulation, and is one of the best examples of a chemical reaction rate which

fulfills the requirements of irreversible thermodynamics in that the rate is proportional to the affinity of the reaction.

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Recent Developments in Semiconductors

This paper will provide an outline of the present state of semiconductor research, and suggest a number of future trends. The topics to be discussed will be divided into: physics of semiconductors, materials research, device research, and systems research. Because of the limitations of space, it will be impossible to define and describe all the terms used in the paper; it will be assumed that the reader has a familiarity with the semiconductor field and its basic terms (*1–4*). We shall only comment that semiconductors are crystalline materials having generally a low conductivity that is highly sensitive to light, temperature, and to impurities in the crystal. Because of these properties semiconductors have become the testing ground for important theories in solid-state physics, and semiconducting devices are becoming so important commercially that they dominate the whole field of electronics.

Generally speaking, semiconductor research in the true sense began with the application of quantum theory to the solid state through the studies of Heisenberg, Sommerfeld, Fermi, and others in 1928; the specific application to semiconductors and the energy level picture was made by Wilson in 1930. An even greater stimulus to research was given by the invention of the transistor in 1948. Because of the tremendous practical importance of the electrical properties of semiconductors, theory and practice have always gone hand in hand in this field.

Although much has been learned in the past about the physics of semiconductors, new developments are still coming thick and fast and in the materials area, there is still tremendous need for progress. For many applications and to observe many interesting properties, semiconductors must be prepared with a purity and a structural perfection greatly exceeding that attainable in other materials. To produce transistor action, for example, silicon and germanium purer and more perfect than any other known materials are regularly being manufactured for commercial production.

There are literally thousands of semiconducting compounds possible, among both the inorganic and the organic compounds, but only a handful have been prepared with any degree of purity and perfection. The proper degree of understanding of the structure, the quantum mechanical band properties, and the nature of interactions between the various basic particles in a given material is a tremendously difficult objective to attain. Even with silicon and germanium we have only approached this level; we have not realized their full possibilities. Thus the surmounting of these problems forms a great challenge to the field of semiconductor research and, in fact, to the whole fields of physics and chemistry. We can truly say that this field remains, relatively speaking, in its infancy.

In addition, the growing importance of semiconductor devices is leading to even more challenging problems of fabrication to produce better, cheaper, and more reliable devices. The problems of miniaturization and multiplexing of devices have already challenged our knowledge of fabrication techniques and our knowledge of the materials themselves to an extent that will keep research men in this field busy for years.

As sophistication grows in this field, "molecular engineering" looms over the horizon as the ultimate challenge in this field, fusing the problems of materials fabrication, device research, and systems design into a single integrated problem.

Presented as part of the Symposium on Chemistry of the Solid State before the Division of Chemical Education at the 138th Meeting of the ACS, New York, September, 1960.

Physical Research on Semiconductors

It is an interesting fact that most of the basic phenomena of semiconductors were known by 1932, and indeed, practically all of the basic particles of solids had been defined and discovered by that time:

Electrons.
Positive holes, i.e., empty levels in the band of energy levels normally filled by electrons. Electrons and holes are the basic electrical carriers in semiconductors.
Phonons, or the "particles" of lattice vibration.
Photons, or the particles of electromagnetic energy.
Excitons, or coupled electron-hole pairs, similar, in a way, to hydrogen atoms.
Polarons, or electrons accompanied by a strain field in the lattice.

Even though these particles are "old" we are still learning much about them.

The theory of atomic structure, of the formation and interaction of these particles, and the experimental catalogue of the interactions of these particles forms to a great extent the subject of the physics of semiconductors.

The conventional theory of semiconductors has been primarily established for perfect crystals with few if any disorders or imperfections, in spite of the fact that it is extremely difficult to produce such perfection. On the other hand, the existence of "amorphous" semiconductors such as liquid selenium, and other melted semiconductors, is causing a redirection of attention to the very imperfect semiconductors. This tendency could lead to a revision of the basis of semiconductor research and will undoubtedly be an active field for many years. It is a development being led by the Soviet scientists associated with the late A. F. Joffe.

On the other hand, the band theory for perfect crystals also has some drawbacks because of the simplifying assumptions which had to be made in it to simplify the mathematics. Efforts are continuing on the task of producing a better band theory so as to increase our understanding of silicon, germanium, and the other nearly-perfect semiconductors.

Among the materials about which new band structure results are appearing are gallium arsenide, bismuth telluride, graphite, and tellurium. Regarding the latter, it appears that the long history of the mysterious double reversal of the Hall effect of tellurium (dating back at least to 1934) can now be explained in terms of two types of holes in the material and in terms of the variations in their properties with temperature, leading first to n-type Hall effects then a reversal back to p-type.

High-pressure studies are being particularly useful in these new programs for bringing out general features of the band structure. Most materials, such as germanium, have a complicated structure in both conduction and valence bands which is seen only dimly in ordinary transport experiments. A new technique is needed to bring the structure out. High-pressure, by altering the interatomic spacings, can alter relatively to each other the effects of the various crystal directions. Results based partly upon such studies and partly on quantum mechanical calculations for gallium arsenide indicate that the conduction band minimum is at the center of the zone (000) and that there are also ellipsoids oriented along the (100) axes, as in the case of silicon but higher by 0.38 in energy than the minimum at (000). These same theoretical results indicate that longitudinal optical lattice vibrations are responsible for the electrical resistivity and mean free path of gallium arsenide at high temperatures.

Among the many important semiconductors about which very little is known in terms of band structure are silicon carbide, copper(I) oxide, zinc sulfide, cadmium sulfide, lead telluride, and lead sulfide. There remains a tremendous amount of work ahead in the sophisticated study of these materials.

Properties of electrons and holes have been thoroughly studied since the days of the transistor, including studies of conductivity, Hall effect, magnetoresistance, thermoelectric effects, rectification, transistor properties, and others. The interaction effects mentioned above are typified by scattering phenomena, such as the problem of mean free path, the distance an electron can travel through the solid crystal without being deflected by a phonon, or lattice vibration. Other interaction phenomena include photoconductivity, which is caused by absorption of light to form electrons and holes, thereby leading to electrical conductivity.

Among the studies of greatest interest at the present time are those on the "exciton." This is the particle representing the bound coupling of an electron and a hole. Although its existence was in doubt for many years after its prediction in 1932, recent studies on photoelectric emission, secondary emission, and photon absorption and photoconductivity have confirmed that the exciton exists. The trend in this field will be for the further study of excitons in germanium, silicon, indium antimonide, cadmium sulfide, and other materials. No practical applications of the exciton are known. Its effects are seen, however, in thermoelectric and optical properties.

The interaction of magnetic fields with the energy levels in solids and with the moving particles in solids continues to be an active area of research. Just as in the early days of spectroscopy the establishment of the basic energy levels of the atoms was followed by the study of such effects as the Zeeman effect (that is, the disturbance of the energy levels by a magnetic field), so similar developments are occurring now in semiconductors. These include "cyclotron resonance," the magneto-optical effects, and other related effects on which much work is being done at the present time. This work is stimulating the establishment of new facilities for production of steady magnetic fields in the range of 100,000 gauss to 1 million gauss, as well as of pulsed magnetic fields of even greater magnitude. Such a facility is now being planned at MIT which will stimulate high-field research on semiconductors.

Interest in high-frequency applications such as the transistor and the tunnel diode, to be discussed later, are leading to increased study of both the high-frequency microwave properties and of the far-infrared properties of semiconductors such as silicon and germanium. Although transistors until recently were limited in frequency ranges, the upper limit is now at 1000 megacycle/sec or higher, even in commercial units. Microwave studies of semiconductor properties are now being made up to about 100,000 megacycle/sec. Infrared spectrometers operating at 100–1000 microns,

a wavelength region not used for research until very recently, are now being used more widely. These studies are adding greatly to our knowledge of the structure of the levels introduced by isolated impurity atoms in crystals. For most semiconductors, these deliberately added impurities determine the important properties of the semiconductor.

A brief list of other important areas in which new results can be expected for some time to come includes the following:

(1) Studies of highly impure semiconductors are just beginning to come into their own, because in the past we needed to understand pure semiconductors before we had the insight and perspective to understand the very impure ones. These "semimetals" include bismuth, gray tin, lead sulfide, some ferrites, and highly doped semiconductors of many types, including silicon and germanium.

(2) The surface properties of semiconductors are reasonably well understood for some materials, but many problems remain. These problems are still extremely important for determining the reliability of important semiconductor devices. Understanding of semiconductors has great importance as well for many associated fields, such as heterogeneous catalysis.

(3) Low temperature studies are of great interest, particularly for understanding of the phonons and other lattice properties. Especially for space applications and computing systems, low-temperature phenomena in semiconductors have considerable practical implications.

Materials Research

Semiconductor research has to a great extent made progress after the development of materials having new stages of refinement and purity. Transistor action, for example, is impossible in the grade of germanium available before World War II.

Such improvements in materials depended upon many factors, including the development of methods of containing and refining. Progress on silicon, for example, was greatly advanced by the development of the "floating-zone" method in which the material was held in a "skin" formed by its own surface tension.

At the present time the problems of producing germanium and silicon are to a great extent solved. The trend is for the same approaches that were so successful in these materials to be applied to new materials having improved or specialized properties.

Gallium arsenide, a grayish metallic-looking semiconductor, is one into which much of the effort in materials is going at the present time; if efforts are successful, within a few years this material may be almost as widely applied as silicon and germanium. It is particularly suitable for high speed switching diodes, for tunnel (Esaki) diodes, and for solar batteries. There is a prospect that we may be able to develop satisfactory transistors using this material.

Although germanium and silicon make satisfactory transistors, we would still like transistors (*a*) to have higher temperature response, (*b*) to have higher frequency response, (*c*) to be more reliable and, (*d*) to be cheaper. Gallium arsenide promises to be more suitable for the first two requirements, although its promise is questionable on the last two.

Even farther in the future is the development of *very* high temperature transistors, which can in principle be made of semiconductors such as gallium phosphide and silicon carbide. If we could solve our present problems of making these two materials, we could probably make good transistors that would operate at a red heat. Such transistors would be extremely useful in space applications, in many military applications, and for power applications where high temperature performance also is needed. Although much effort has gone into gallium phosphide and silicon carbide, results have been disappointing and effort is waning.

Thermoelectric research is one of the materials research areas in which tremendous efforts are being made. This effort is based upon the hypothesis that power conversion using thermocouples and refrigeration, either on a specialized electronic level or for general home and business use, is practical, provided the proper materials can be found. In this case no new physics or devices are likely to be involved; the search is based on the need to improve materials parameters.

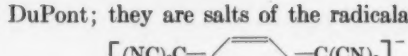
As a result of this effort, numerous combinations of the selenides, tellurides, and sulfides of many different elements are being studied with respect to their critical properties for these applications, especially thermal conductivity in the temperature range of importance and electrical properties such as mobility and thermoelectric power. Some progress is being achieved, and under certain circumstances power conversion efficiencies of 20% are now possible, as well as refrigeration to 70–80° C below room temperature. In general, however, power converters using thermoelectricity are actually being made for special purposes not exceeding 1–2% over-all efficiency. Rare-earth sulfides (gadolinium sulfide) show promise.

In the past few years, the over-all improvement of these devices has been slow but steady. It is probably, however, going to require a "breakthrough" to a new level of performance before widespread commercial application is achieved. If such a breakthrough does arrive, the commercial power conversion and refrigeration fields may be subjected to the same kind of revolution caused by transistors in the electronics industry. To date, such hopes of revolutionary changes have not been realized in the thermoelectric field.

Basic to all improvement in the better materials is the understanding of materials imperfections and of ways to reduce or eliminate their effects. For the past few years attention has concentrated on the *dislocation*, a line of imperfections running like a thread through many crystals. Some crystals have 10,000 to 100,000 or more such dislocations through each square centimeter. Recent research on silicon and germanium has led to production of dislocation-free crystals. This has amounted to a major achievement in materials research. We are now in a position to go ahead and study residual effects due to point defects and "prismatic loops."

It has long been hoped that organic semiconductors would someday join materials such as silicon and germanium in technological importance. Attention has focused on compounds such as copper and magnesium phthalocyanine. Recently an interesting new set of compounds having higher electronic conductivity than any others reported has been announced (*5*) by workers

at DuPont; they are salts of the radicalanion



These "tetracyanoquinodimethans" have an electron density of one free electron per molecule, and a resistivity of the order of 0.2–1000 ohm cm, depending on direction. These are thousands of times lower than that attained in most other electronically conducting organic materials. The electron mobility seems to be very low, although no complete data have been published. The thermoelectric power of -100 μv/°C is characteristic of a good metallic conductor.

Further publication of results on these interesting new materials will be eagerly awaited by many.

Device Research

New devices arise from the discovery of new effects in known materials or from use of new effects with newly developed materials. The transistor, for example, was made possible by the discovery of a new phenomenon, the so-called *injection* of minority carriers, so that *both* holes and electrons, rather than a single carrier, could be operative in a semiconductor.

Recent new devices which have altered the picture of semiconductor applications are headed by the tunnel or Esaki diode (*6*) and the parametric diode.

The Esaki diode utilizes an old quantum mechanical effect known since 1928, the penetration of high but very thin barriers by electrons. It makes possible construction of negative resistance diodes with extremely high frequency response, up to 3–5 thousand megacycle/sec. In structure the Esaki diode is similar to a microwave mixer diode. Such Esaki (or tunnel) diodes do not replace transistors or tubes, but require utilization in new types of circuits in order to be used as amplifiers, oscillators, or switching elements.

To date, commercial Esaki diode products utilizing germanium, silicon, and gallium arsenide have been announced. During the next few years it is expected that the gallium arsenide type in particular will be perfected and incorporated in several specialized systems. It is impossible to predict at the present time, however, whether these applications will be few in number or whether they will result in changing the nature of electronics, and affect the role of the transistor. They do have some extremely important advantages over the transistor besides their frequency capability, including less sensitivity to temperature, surface conditions, and nuclear radiations. Unfortunately, their rate of application has not been as rapid as expected, primarily because of their low power-handling capabilities and difficulties in designing them into circuits. Some computer designers still retain, however, strong faith in the Esaki diode.

Parametric diodes are point-contact or small-area junction diodes; because their capacity depends upon the voltage, they permit modulation, mixing, and amplification through the intermediate agency of a pumping signal of different frequency.

Such diodes have now been applied in extremely high frequency systems and have been shown to give good amplification and low noise. Gallium arsenide, silicon, and germanium all show the basic effects involved, but gallium arsenide appears to give the best frequency response.

Systems

The absorption of the transistor and related devices into semiconductor and electronic technology is proceeding at a rapid rate. The modifications of circuit and system design to make use of the peculiar operating conditions of the transistor have now extended to many commercial and military systems. This has led to a proliferation of device types, so that a large catalogue is needed to identify these types. It is expected that some simplification of models and types must follow if replacement and maintenance of systems in the field is to be easy, and if designers and inventors are not to be handicapped by a welter of nearly identical types. The semiconductor industry is now operating at the rate of about 400 million dollars per year.

The module concept is increasing in importance, both with respect to standard multiples which for maintenance purposes can be easily replaced in the field, and with respect to the miniaturization process which we expect will be an increasingly important aspect of electronic technology.

Much publicity is being given at the present time to systems concepts, sometimes called "molecular electronics," involving the incorporation by unit processes of a wide variety of devices in a continuous system, without connectors or wires, embodying the entire function now available only in a wired assembly of components.

The promise is great in these areas but the difficulties of achieving such integrated circuit functions are such that many years may go by before complete systems based on these principles can develop beyond the most rudimentary applications.

At the present time, it appears that integrated combinations of diodes, capacitors, and resistors *can* be made having circuit capabilities. The number of functions of which they are capable, however, is very limited, as in the multivibrator and other circuits similar to it. Even if such functions can be utilized in practical systems, even in this elementary case, it may be at least five years before reliable processes and systems are developed.

Basic research will undoubtedly, sooner or later, fill in many of the gaps which at the present time make reliable integrated systems impracticable. In any case the role of semiconductors in electronic technology continues to expand, and even more important developments in the future may be expected than we have seen in the past.

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The Luminescence of Inorganic Crystals

Luminescence is a quite general phenomenon of light emission in excess of thermal radiation. In contrast to the Raman effect, Compton scattering, and Cherenkov emission, luminescence involves a time delay of emission after excitation which is long compared to the period of the emitted radiation, λ/c or approximately 10^{-15} seconds. Luminescent emission involves optical transitions between electronic states characteristic of the radiating material. The lifetime of the emitting state may be as short as 10^{-8} seconds or as long as 10^{-1} seconds depending on the nature of the electronic transition. In addition, if metastable or trapping states are involved, thermal activation may be prerequisite to emission and this afterglow or phosphorescence may persist for days. Energetic electrons, γ- or X-rays, ultraviolet radiation, or applied electric fields excite luminescence in suitable materials. Because the spectrum of each emission band of most materials is independent of the nature of the excitation and since excitation by ultraviolet radiation involves the simplest mechanism of excitation, we shall confine this review to photoluminescence.

Although luminescence occurs in gases, liquids, and solids—both inorganic and organic—we shall confine this review to inorganic crystals because of the scope and emphasis of this symposium. We shall not attempt to make this review comprehensive but rather shall discuss representative inorganic crystals which illustrate the basic ideas involved in interpreting photoluminescence.

Chemical impurities and crystalline imperfections are the dominant sites for luminescence in inorganic crystals. The luminescent sites or activators are usually monatomic impurities or imperfections, but in some cases they can be diatomic. Many luminescent crystals or phosphors belong to the same class of solids as do crystals which are semiconducting and photoconducting. In fact, in some phosphors the impurities which are responsible for luminescence are also involved in semiconductivity and photoconductivity.

We shall first consider monatomic impurities in alkali halide crystals which have been extensively investigated in a tight binding approximation, by considering the free ion states of the activator perturbed by crystalline interactions. Transition metal activators, particularly dipositive and tetrapositive manganese, are then considered with the aid of crystal field theory. More complex phosphors such as the calcium halophosphates activated by manganese and antimony are discussed, and finally the binary semiconducting phosphors such as zinc sulfide are considered in some detail.

Presented as part of the Symposium on Chemistry of the Solid State before the Division of Chemical Education at the 138th meeting of the ACS, New York, September, 1960.

Monatomic Impurities in Alkali Halides

Impurities and imperfections in alkali halide crystals have been extensively investigated for many years. Monopositive thallium substituted at cation sites in dilute concentration in potassium chloride probably comprises the simplest and most exhaustively investigated activator system. Two decades ago, it was proposed that states of Tl^+ perturbed by crystalline interactions are responsible for the luminescence (*1*). The activator system was identified as Tl^+ substituted at K^+ sites, as illustrated in Figure 1. The principal excitation and emission bands were attributed to transitions between the ^1S ground state with the $6s^2$ configuration to perturbed $^3P_1^0$ and $^1P_1^0$ states with the $6s6p$ configuration. By introducing simplifying ideas on the crystalline interactions and atomic rearrangements, the excitation and emission spectra associated with the long wavelength impurity absorption band in KCl:Tl were calculated a decade ago (*2*). The energy of the $6s^2$ ^1S state of the Tl^+ in the band structure of KCl can be computed by considering the Born-Haber type cycle:

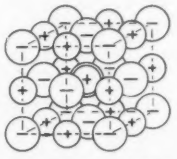

Figure 1. Structure of luminescent center in KCl:Tl.

$$\begin{array}{ccc} Tl^+(g) + KCl(s) & \xrightarrow{I} & Tl^{++}(g) + KCl(s) + e(g) \\ \downarrow \Delta E & I' & \downarrow \Delta E' - F \\ KCl{:}Tl(s) + K^+(g) & \rightarrow & KCl{:}Tl^{+2} + K^+(g) + e(s) \end{array}$$

where I is the second ionization energy of Tl, F is the electron affinity of KCl in the lowest conduction state, ΔE and $\Delta E'$ are the changes in crystal energy on substituting Tl^+ and Tl^{+2}, respectively, for K^+ in KCl, and I' is the ionization energy of Tl^+ in KCl and is, therefore, the energy from the $^1S_0$ state of Tl^+ to the conduction band. Similar calculations can be made for Tl^+ in excited electronic states. The band model for the energy levels of KCl:Tl is shown in Figure 2.

The energies of the localized states of Tl^+ in KCl:Tl are functions of the atomic coordinates of the crystal, and since the neighboring ions will interact differently with the Tl^+ in its ground and excited states, the transition energy between these states will depend on the coordinates of the ions comprising the activator system. In other words, although the activator is an

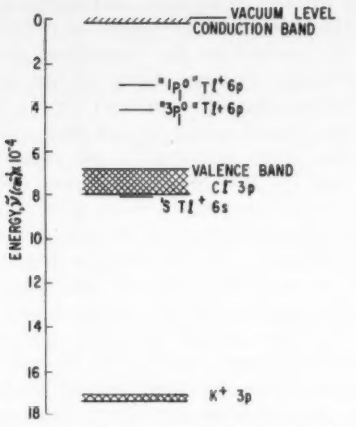

Figure 2. Band theory model for energy level structure of KCl:Tl.

isolated Tl^+ at a K^+ site, the activator system is like a polyatomic molecule because of the coupling between the Tl^+ and the KCl crystal. These effects are evident in the configuration coordinate model shown in Figure 3. The configuration coordinate model is based on the adiabatic approximation according to which the wave function $\psi(r, q)$ for a state of the impurity system can be written:

$$\psi(r, q) = \phi(q)\varphi(r, q). \qquad (1)$$

The electronic wave function $\varphi(r, q)$ is a function of the electronic coordinates r and is smoothly modified by changes in the positions q of the nuclei whose state of motion is described by $\phi(q)$. In the actual calculation, the harmonic approximation was also made, that is, the dependence of $\varphi(r, q)$ on q was neglected. The energies of the ^1S and $^3P_1^0$ states of Tl^+ are shown as a function of the symmetrical radial displacement of the six nearest-neighbor Cl^-. The other ions are allowed to relax to equilibrium positions for each value of the configuration coordinate.

The absorption and emission spectra at ordinary temperatures can be determined from the configuration

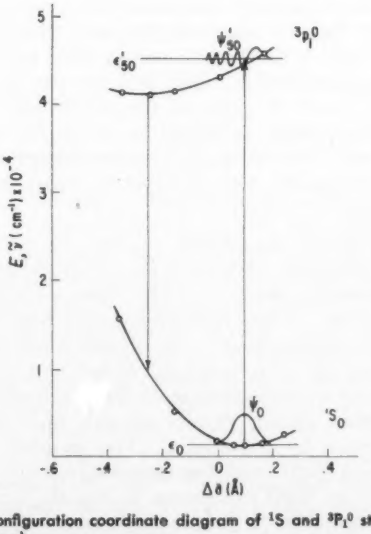

Figure 3. Configuration coordinate diagram of ^1S and $^3P_1^0$ states of Tl^+ in KCl (Williams).

coordinate curves semiclassically, that is, the configurations of the initial state are weighted by a Boltzmann function and the optical transitions are constrained to vertical transitions in accordance with the Franck-Condon principle. At low temperatures the zero point energy associated with the vibrations of the activator system must be taken into account. The spectra must, therefore, be determined quantum mechanically, that is, by weighting the vibrational levels of the initial state by a Boltzmann function and multiplying by the matrix elements for transitions between the vibrational levels for the initial and final states. Representative vibrational levels and wave functions are shown in Figure 3. The spectra $E_{\tilde{\nu}}$ at the temperature T, including the effect of zero point energy, can be expressed in the form (3):

$$E_{\tilde{\nu}} = (K/2\pi kT)^{1/2}\exp\left[-Kq^2/2k\theta\coth\left(\frac{\theta}{T}\right)\right]\frac{dq}{d\tilde{\nu}} \qquad (2)$$

where K is the force constant for the activator system in the initial state, q is the displacement in the configuration coordinate from the equilibrium value for the initial state, $\tilde{\nu}$ is the difference in energy in wave numbers of the configuration curves at q, and $k\theta$ is the zero point energy.

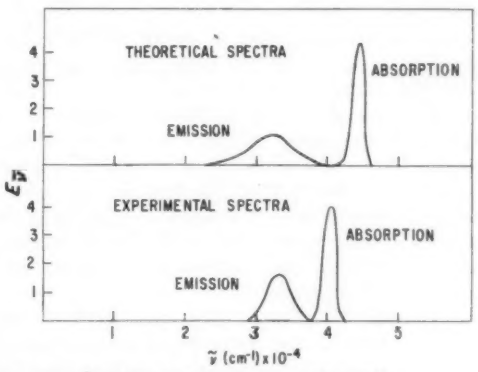

Figure 4. Spectra for $^1S \rightleftarrows {}^3P_1^0$ transitions of Tl^+ in KCl.

The experimental and theoretical spectra for 300°K are shown in Figure 4. The widths of the absorption and emission bands at 80°K are found both experimentally and theoretically to be approximately one-half their respective 300°K band widths and further lowering of the temperature does not appreciably reduce the widths. Hydrostatic pressure favors transitions characterized by smaller interatomic distances. This effect can be treated theoretically by an additional term in the exponential of equation (2) (4). The long wavelength absorption band in KCl:Tl is displaced 80 cm^{-1} to smaller transition energy by 2000 atm in accordance with theory. The sign of the spectral shift with pressure verifies that the equilibrium interatomic spacing for the excited state is smaller than for the ground state.

Quite recently, a similar theoretical analysis has been completed for NaI:Ag and confirmed by a rigorous quantum mechanical calculation of the interactions of the Ag^+ with the NaI crystal (5). In this phosphor the luminescence is attributed to the $4d^{10}\ ^1S \rightleftarrows 4d^9 5p\ ^3D$ transitions of Ag^+ perturbed by crystalline interactions. The widths of the absorption and emission bands and the Stokes shift between absorption and emission were shown to result from the difference in radial charge

densities of the ground and excited states of the activator principally through the Coulomb overlap interaction with the neighboring ions. This is also the case for KCl:Tl.

In addition to the theoretical investigations on the absorption and emission spectra corresponding to the $^1S \rightleftarrows {}^3P_1^0$ transitions of KCl:Tl, the problem of the ratio of oscillator strengths of the two principal absorption bands involving the $^1S \rightarrow {}^3P_1^0$, $^1P_1^0$ transitions has received attention. The relative intensities of these transitions are determined by the mixing of the $^3P^0$ and $^1P^0$ pure spin states by spin-orbit interaction. By using the free ion spin-orbit coupling constants and by determining the energy separation of the pure spin states from the experimental transition energies, the relative intensities of the absorption bands were computed and found to be in accord with experiment (*6*). The effect of spin-orbit interaction on the configurative coordinate model has been considered and a new emission band in the spectral region of the long wavelength absorption band was thereby predicted and experimentally verified (*7*). The Jahn-Teller effect which removes the orbital degeneracy of the impurity states by non-cubic distortions of the lattice, has also been invoked to explain some characteristics of the spectra of KCl:Tl (*8*).

The properties described in detail for KCl:Tl are also evident qualitatively in other inorganic crystals. Neutral Hg which is isoelectronic with Tl^+ can be dispersed atomically in the zeolite harmotome to yield luminescence according to the $6s^2\ ^1S \rightleftarrows 6s6p\ ^3P_1^0$ transitions (*9*). The homologous series of impurities: Ga^+, Ge^{+2}, In^+, Sn^{+2}, Pb^{+2}, as well as Tl^+, activate the alkali halides to yield luminescence according to the transitions, $s^2\ ^1S \rightleftarrows sp\ ^3P_1^0$, $^1P_1^0$ (*10*). These transitions are also involved in the luminescence of some of the more complex phosphors.

It should not be inferred from the extensive investigations on KCl:Tl and related phosphors that there remain no unsolved problems regarding the luminescence of these relatively simple materials. Among the unsolved problems are the identifications of the impurity system and electronic states responsible for a longer wavelength emission band. The origin of the trapping states which dominate the phosphorescence also remains inconclusive.

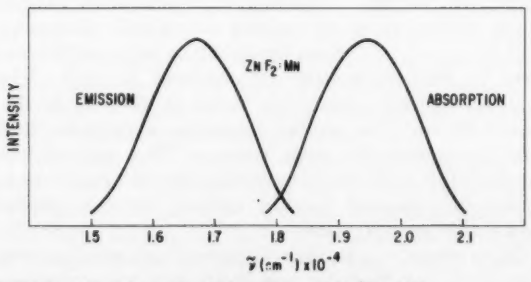

Figure 5. Absorption and emission spectra of Mn^{+2} in ZnF_2.

Transition Metal Activators

A variety of inorganic crystals become luminescent when certain transition metal ions are dissolved in them. The electronic transitions involved are intercombination transitions within the 3*d* shell, and therefore, the tight binding approximation is valid in explaining the spectra. In contrast to the transitions $s^2 \rightleftarrows sp$ previously discussed, no large change in the radial charge density distinguishes the excited from the ground state for transitions within the 3*d* shell. There may, however, be large changes in the angular charge densities, and for this reason there are differences in interaction with the crystal for the ground and excited states and a dependence of the transition energy on the atomic coordinates of the neighboring ions. This interaction is essentially a crystal field theory problem. The activator system can be regarded as a transition metal ion complex. Each electronic state of the $3d^n$ configuration will have a particular dependence on the crystal field splitting parameter Dq and the width of the absorption and emission bands will depend on $d(h\nu)/d(Dq)$, where $h\nu$ is the transition energy (*11*). All the states of the $3d^n$ configuration have the same parity; therefore, unless the activator site does not have a center of symmetry, the transitions will be forbidden. In addition, many of the transitions of interest are also forbidden because of a change in multiplicity.

Dipositive manganese is probably the most widely distributed activator ion in inorganic crystals. Zn_2SiO_4, $MgSiO_3$, $CaSiO_3$, $Cd_2P_2O_5$, $Zn_3(PO_4)_2$, ZnF_2 and ZnS are among the important phosphors activated by Mn^{+2}. The electronic configuration is $3d^5$, and the ground state, in accordance with Hund's rule of maximum multiplicity, is ^6S. In many crystals, the Mn^{+2} site has octahedral symmetry; in some, tetrahedral. Since the former has a center of symmetry and the latter has not, the lifetime of the excited state will as a rule be longer for the Mn^{+2} at octahedral sites.

Let us consider, for example, ZnF_2:Mn. Both ZnF_2 and MnF_2 have the rutile structure, and the phosphor is a mixed crystal consisting of a few mole per cent of MnF_2 in ZnF_2. Since the nearest neighbor F^- of the Mn^{+2} are approximately at the corners of a regular octahedron, we can approximate the crystal field as cubic. The ^6S ground state is not split by the cubic field and is labeled $^6A_1$; the lowest lying excited free ion state, which is the ^4G state, is split by the cubic field and the lowest lying component is labeled $^4T_{1g}$. It has been proposed that the transitions $^6S(^6A_1) \rightleftarrows {}^4G(^4T_{1g})$ are responsible for the long wavelength absorption band and for the emission of ZnF_2:Mn (*12*). A value of Dq of 900 cm^{-1} for the equilibrium atomic configuration of the $^6A_1$ state and of 1300 cm^{-1} for the equilibrium configuration of the $^4T_{1g}$ are consistent with the spectra which are shown in Figure 5.

Tetrapositive manganese is also an activator in several inorganic crystals. In contrast to Mn^{+2}, the luminescent emission of Mn^{+4} has a characteristic fine structure. These transitions occur between states of the $3d^3$ configuration. In several materials, manganese can be introduced in either the di- or the tetrapositive state depending on the composition of the vapor phase during crystal growth and on charge compensation by impurities. The simplest of these materials is MgO, and the emission spectra of Mn^{+2} and Mn^{+4} in MgO are shown in Fig. 6. In order to prepare MgO:Mn^{+4}, the phosphor must be prepared in

an oxidizing atmosphere and also with Li^+ for charge compensation (*13*). Two Li^+ plus one Mn^{+4} substitute for three Mg^{+2}.

Another inorganic material which can be activated with Mn^{+4} is Li_2TiO_3. This phosphor is of interest because it can be prepared in an ordered or in a disordered structure, and the effect of structure on the luminescence is clearly evident (*14*). In the disordered phase which can be attained by thermal quenching or stabilized by mixed crystal formation with MgO, the Li^+ and Ti^{+4} are randomly distributed over the cation sites in the rock salt structure. In the ordered phase which is attained with slow annealing, the structure remains cubic but the Li^+ and Ti^{+4} are ordered among the cation sites. The Mn^{+4} substitutes for Ti^{+4}, which in the ordered structure are at octahedral sites but in the disordered structure are at sites without a center of symmetry. In accordance with the earlier remark on the applicability of the parity selection rule, the lifetimes of the emitting state of Mn^{+4} in the ordered and disordered Li_2TiO_3 are, respectively, 1.2×10^{-3} and 0.3×10^{-3} seconds.

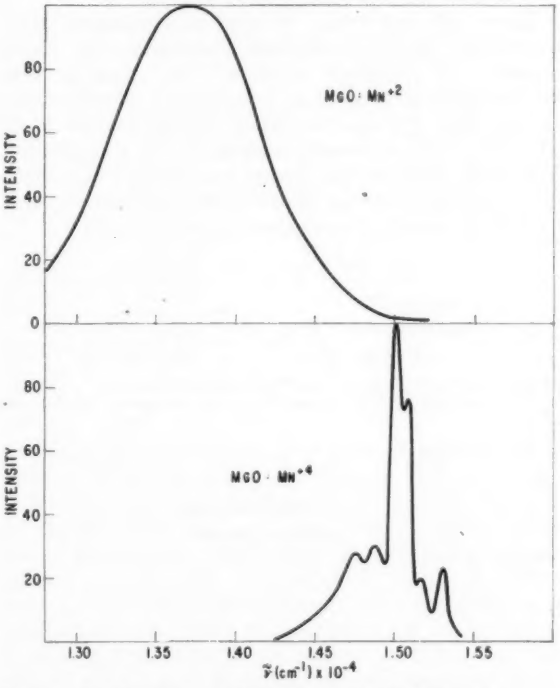

Figure 6. Emission spectra of Mn^{+2} and Mn^{+4} in MgO (Prener).

In addition, because of the inhomogeneity among the Ti^{+4} sites in the disordered Li_2TiO_3 the afterglow is non-exponential and the characteristic emission fine structure vanishes. The emission spectra of the ordered and disordered $Li_2TiO_3:Mn^{+4}$ are shown in Figure 7.

An inorganic luminescent crystal which has been quite recently investigated as a high intensity light source with unusual properties is Al_2O_3 activated with Cr^{+3}. The activator Cr^{+3} is isolelectronic with Mn^{+4} and has the same energy level structure. However, excitation of $Al_2O_3:Cr^{+3}$ in the broad absorption band corresponding to the $^4A_2 \rightarrow {}^4F_2$ transition is followed by efficient transfer to the ^2E state. The emission corresponding to the transition $^2E \rightarrow {}^4A_2$ is a quite narrow line because $d(h\nu)/d(Dq)$ is very small. Because of the narrowness of the emission it is possible to achieve a sufficient emission radiation density per wavelength interval so that the induced transition probability

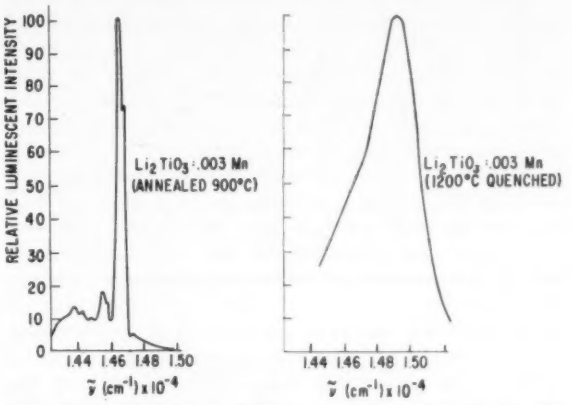

Figure 7. Emission spectrum of Mn^{+4} in annealed and quenched Li_2TiO_3 (Lorenz and Prener).

becomes comparable or large compared to the spontaneous transition probability and the emission becomes coherent (*15*).

Complex Ionic Phosphors

Calcium halophosphate activated by manganese and antimony is the most widely used photoluminescent material. The formula is $3Ca_3(PO_4)_2.CaX_2$:Mn, Sb where X = F, Cl; and the structure is the same as the mineral apatite. There are two structurally different Ca^{+2} sites. Each of the four type I Ca^{+2} sites in the unit cell is on a trigonal symmetry axis parallel to the optic axis and has six O^{-2} nearest neighbors, whereas each of the six type II Ca^{+2} sites is in a reflection plane perpendicular to the optic axis with no other symmetry and has as nearest neighbors five O^{-2} and one F^-.

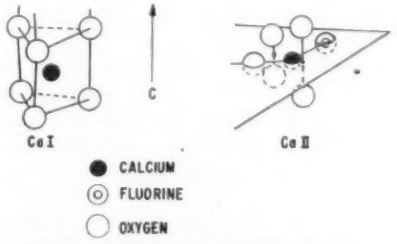

Figure 8. Activator sites in calcium fluorophosphate.

These sites are shown in Figure 8. The emission spectrum of a representative phosphor is shown in Figure 9.

The manganese responsible for the orange emission has for a decade been attributed to Mn^{+2} at the type II Ca^{+2} site; however, quite recent measurements of the polarized luminescence of single crystals indicate that Mn^{+2} at type I Ca^{+2} sites is the activator (*16*). The orange emission is consistent with the $^4G \rightarrow {}^6S$ transition of the $3d^5$ configuration of Mn^{+2} perturbed by the crystal field.

Because the antimony in the halophosphate phosphors is tripositive, there is the problem of charge compensation of the Sb^{+3} substituted at Ca^{+2} sites.

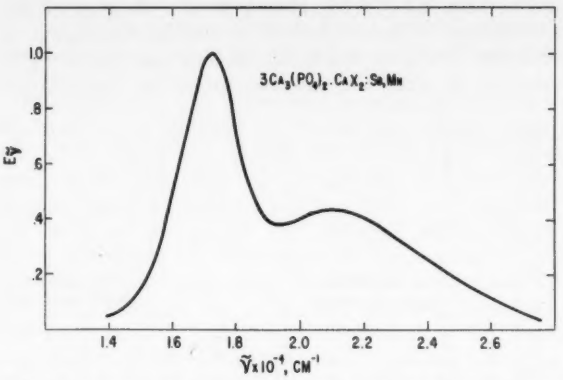

Figure 9. Emission spectrum of representative halophosphate phosphor.

If we attribute the blue emission (Fig. 9) to Sb^{+3} at the type II Ca^{+2} sites, charge compensation can be achieved by concurrent substitution of O^{-2} at the nearest-neighbor X^- site. This identification is consistent with the chemistry of halophosphate phosphors, including a lower X^- content than corresponds to the stoichiometry of the pure halophosphate (*17*). In any case, the antimony impurity is a substitutional impurity with an excess positive charge and is charge compensated by a negatively charged impurity or imperfection. The antimony and the compensating impurity or imperfection will be associated into ion pairs because of the coulombic interaction between them.

Since Sb^{+3} has an electronic structure similar to Tl^+, the theoretical work on KCl:Tl can be applied qualitatively to Sb^{+3} in the halophosphates. In both ions the ground state is the ^1S state with the s^2 configuration, and the excited states are the $^3P_1^0$ and $^1P_0^0$ states with the *sp* configuration. The KCl:In and the $3Ca_3(PO_4)_2.CaX_2$:Sb are even more closely related since In^+ and Sb^{+3} are precisely isoelectronic. For example, the mixing by spin-orbit interaction of the $^3P^0$ and $^1P^0$ states are more nearly the same for In^+ and Sb^{+3} than for Tl^+ and Sb^{+3}.

However, because of the difference in charge of the Sb^{+3} and the Ca^{+2} it replaces and because of the excess charge of the compensating impurity, another type of transition must be considered. For example, let us consider the diatomic impurity system consisting of Sb^{+3} at a type II Ca^{+2} site and O^{-2} at the nearest-neighbor X^- site. This ion pair and those characterized by larger impurity distances have features similar to the donor-acceptor pairs in zinc sulfide which we shall discuss in the next section. If we assume halophosphates are ionic crystals, we can consider classical electron transfer processes in the $Sb^{+3} - O^{-2}$ diatomic impurity.

$$Sb^{+3} - O^{-2} \rightleftharpoons Sb^{+2} - O^-$$

Since the Madelung constants for the various sites of the apatite structure have not been evaluated, it has not been possible to calculate the energies for the above transitions. It is, however, simple to calculate the difference in energy for the above transition and the intrinsic transition:

$$Ca^{+2} - O^{-2} \rightleftharpoons Ca^+ - O^-$$

which can, on the ionic model, be identified with the optical absorption edge of the pure halophosphate. From this calculation, we find that electron transfer states of the $Sb^{+3} - O^{-2}$ pairs are to be expected in the same energy range as the excited $^3P_1^0$ and $^1P_1^0$ atomic states of Sb^{+3}. The electron transfer states, in contrast to the atomic states, are coupled to the valence and conduction band edges.

The correct crystal states of the antimony activator system will have the characteristics of both the atomic and of the electron transfer states. In other words, configuration interaction between the atomic and transfer states will occur. The localized atomic rearrangements responsible for the Stokes shift of the absorption and emission spectra of the antimony activator are probably determined by the atomic-like part of the impurity wave function, whereas sensitization of the manganese emission is probably determined by the diffuse electron transfer part of the wave function for the excited antimony activator system. In view of these complexities it is not surprising that the halophosphate excitation spectrum, which is characteristic of the antimony activator system, is as complex as shown in Figure 10.

There are exceptions to the generalization that impurities and imperfections dominate the luminescence of inorganic crystals. For example, the luminescence of magnesium tungstate is characteristic of the WO_4^{-2} group perturbed by the crystal field. The WO_4^{-2} are sufficiently separated and well-shielded from each other so that energy transfer between them does not occur, except above room temperature, and each WO_4^{-2} can be described as a localized system.

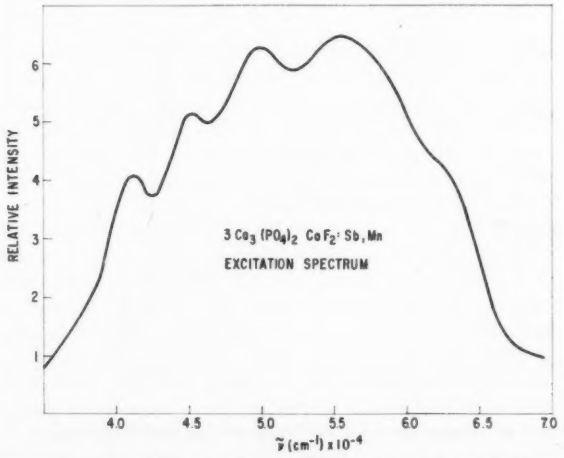

Figure 10. Excitation spectrum for antimony emission of calcium fluorophosphate (Johnson).

Covalent Phosphors

Binary compounds of Group IIB and VIB elements of the periodic table, such as zinc sulfide, have been considered both as ionic and as covalent crystals. The local tetrahedral coordination characteristic of the wurtzite and zinc blende structures is indicative of non-central forces consistent with the covalent model. On this basis ZnS can be regarded as composed of Zn^{-2} and S^{+2} ions with tetrahedral sp^3 hybridized orbitals. These orbitals, however, will be highly polarized because of the large difference in charge of the

ion cores. In the limit of the ionic model, ZnS is regarded as Zn^{+2} and S^{-2} ions. The correct description obviously lies between the covalent and ionic models; however, the net charge which can be attributed to each ion depends on the boundary that is chosen for each. Fortunately, many of the properties attributable to impurities in the IIB-VIB compounds depend on the difference in charge of the impurity and of the ion replaced, and this difference is usually unambiguous and independent of the ionic or covalent character of the pure crystal.

Group IIB-VIB compounds which contain Group IB or VB activators and Group IIIB or VIIB coactivators comprise a large class of luminescent crystals. These phosphors and the impurities responsible for luminescence are shown in the part of the Periodic Table reproduced in Figure 11. The activator largely determines the emission spectrum, and the coactivator facilitiates luminescence but usually has little effect on the emission spectrum. The role of the coactivator in the chemical preparation of these materials has been interpreted on the basis of charge compensation (*18*).

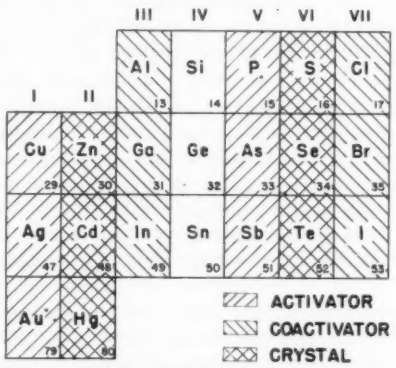

Figure 11. Section of periodic table relevant to activators and coactivators in binary compounds of the zincblende or wurtzite structure.

The energy level structure of these phosphors can be deduced from semiconductor theory (*19, 20*). The orderly arrangement of the activators and coactivators in Figure 11 is also explained. The impurity states are treated as perturbed states of the band structure of the pure crystal. The substitution of activators from Group IB for Zn or Group VB for S perturbs a series of discrete states upward from the valence band because the charge of the impurity core is less than the charge of the core replaced. In the neutral crystal with only activators present, the highest state is empty, that is, contains a positive hole, therefore, the activator, is an acceptor. The substitution of coactivators from Group IIIB for Zn or Group VIIB for S yields a series of discrete states below the conduction band because of the extra core charge of the coactivator. In the neutral crystal with only coactivators present, the extra electron which compensates for the extra core charge is bound in the lowest of these discrete states. The coactivator is, therefore, a donor. The simultaneous introduction of activator and coactivator results in electron transfer from donor to acceptor,

$$D^0 + A^0 \rightarrow D^+ + A^-$$

and the energy is reduced by a large fraction of the band gap. Since the band gaps of these materials is quite large, i.e., 3.7 ev or 85 kcal for ZnS, the interdependence of the solubilities of coactivators and activators in this class of phosphors is understandable.

In those cases where activator and coactivator impurities are not introduced into the crystal in equivalent concentrations, other mechanisms for charge compensation are essential (*21*). At the high temperatures of crystallization where equilibrium must be established, the donors and acceptors are ionized. One mechanism for charge compensation is by free charge carriers. For example, donor impurities may be compensated by conduction electrons. In addition, Group IIB or VIB vacancies or interstitials may act as acceptors or donors and thereby provide charged imperfections for the compensation of charged impurities. For example, donor impurities such as D^+ in the solid MX, may be compensated by metal vacancies V_M^-:

$$D^0 \rightarrow D^+ + V_M^- + M(g)$$

Since the solid MX containing donor or acceptors in equilibrium with a vapor phase consisting of M(g) and X(g) is trivariant, the temperature, pressure, and impurity concentration determine the composition of the solid. By computing the free energy changes for charge compensation by charge carriers and by imperfections, it can be shown that compensation of donor impurities by metal vacancies will dominate if:

$$\ln P_M < \ln\left[{}^1/_4 N_0 kT\left(\frac{m_M}{m_e}\right)^{3/2}\right] + \frac{E_g - E_A - E_M}{kT} \qquad (3)$$

where P_M is the metal pressure in the gas phase, N_0 is the concentration of metal atoms in the solid, m_M and m_e are the masses of the metal atom and of the electron, E_g is the band gap, E_A is the energy of the acceptor level, and E_M is the energy required to form a neutral metal vacancy. In the Group IIB-VIB compounds the metal and non-metal vacancies are double acceptors and double donors, respectively, therefore E_M in equation (3) for this class of phosphors is one half the energy to form a neutral vacancy. For acceptor impurities, compensation by non-metal vacancies occurs in accordance with equation (3) except that subscripts M and A are replaced by X and D. By quite general methods based on the mass action law, the interdependence of the concentrations of charged impurities and imperfections has been formalized (*22*).

The ionized donors and acceptor, either impurities or imperfections, are charged either by electron transfer or by thermal ionization at the temperature of crystallization and therefore interact coulombically and are not distributed at random. Qualitatively, the donor and acceptor are paired similar to ions in solution according to the Debye-Hückel theory. Quantitatively, account must be taken of the fact that the donors and acceptors occupy only lattice sites. The statistical analysis, including this effect, leads to the following expression for the fraction α_i of pairs characterized by the interimpurity distance r_i (*23*):

$$\alpha_i = AcZ_i[\exp(-q_A q_D/Kr_i kT)][\exp(-c\sum_{j=1}^{i} Z_j)] \qquad (4)$$

where c is the concentration of donors and acceptors, Z_i is the number of sites at r_i, q_A and q_D are the charges

on acceptor and donor, K is the static dielectric constant, A is a normalization constant, and T is the temperature below which diffusion over interimpurity distances does not occur. Application of equation (4) to Group IIB-VIB compounds with representative activator and coactivator concentrations indicates that association into pairs must be included in the theory of the luminescence of this class of phosphors.

The activator copper is responsible for several emission bands in zinc sulfide. The infrared luminescence is probably the simplest since it does not involve interimpurity or interband transitions but only intra-acceptor transitions, that is, hole transitions between the ground, excited and ionized states of the Cu^0 acceptor at Zn sites (*24*). The energy levels are shown in Figure 12. In order to attain the proper

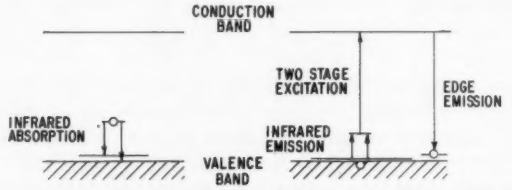

Figure 12. Infrared absorption and emission of Cu^0 in ZnS, and two stage excitation and edge emission.

valence of the copper for infrared excitation and emission, it is evident that the chemical potential for electrons must be lowered to the energy of the ground state of the acceptor. In other words, charge compensation of the Cu^- by sulfur vacancies V_S^{+2} must be minimized. This can be achieved by high sulfur pressure. The chemical equation describing the compensation is for a solid consisting of δ moles of Cu in ZnS:

$$Zn_{1-\delta}Cu^0_\delta S \rightleftharpoons Zn_{1-\delta}Cu^-_\delta (V_S^{+2})_{\delta/2}\, S_{1-\delta/2} + \frac{\delta}{4}S_2(g)$$

If we apply the law of mass action and the conditions for charge and material balance, we find that the infrared intensity I is at low pressures of sulfur:

$$I = K_1[Cu^0] = K_2 P_{S_2}^{1/4} \qquad (5)$$

where K_1 and K_2 are constants. At high pressures of sulfur, all the Cu is in the Cu^0 state and I becomes independent of P_{S_2}. The experimental dependence of I on P_{S_2} is shown in Figure 13. This result verifies

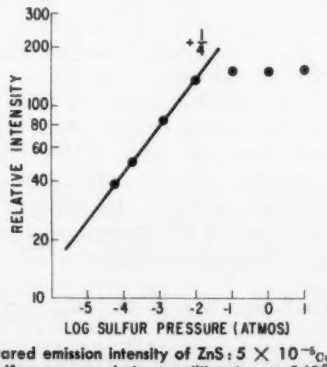

Figure 13. Infrared emission intensity of ZnS: 5×10^{-5} Cu at 196°C as a function of sulfur pressure during equilibration at 940°C (Apple and Prener).

that if hole transitions of the Cu^0 acceptor are responsible for the infrared luminescence, then the compensating imperfection is a double donor. The compensating imperfection is probably a sulfur vacancy; however, an interstitial zinc is also consistent with the data.

A quite striking anti-Stokes luminescence is also observed with copper activated zinc sulfide and cadmium sulfide which exhibit infrared excitation and emission (*26*). The phenomenon involves electron ionization of the Cu^- following hole ionization of the Cu^0, and together these two separate optical transitions yields "edge emission" which consists of narrow bands near the absorption edge of the pure crystal. The two stage excitation is shown on Figure 12. The identity of the impurity or imperfection involved in edge emission remains ambiguous; nevertheless, the two stage excitation is quite unambiguous and confirms the nature and energy levels structure of the copper impurity responsible for the infrared excitation and emission.

With the exception of the infrared luminescence just described, the emission bands of Group IIB-VIB compounds containing Group IB or VB activators and/or Group IIB or VIIB coactivators involve radiative recombination of an electron in a donor or conduction band state with a positive hole in an acceptor state. In the case of ZnS containing only donor impurities, a problem has been the identity of the acceptor or activator involved in the "self-activated" blue emission. It was pointed out earlier in this section that compensation of the donor impurities can be achieved by metal vacancies which are double acceptors. This mechanism of compensation is dependent on the pressure of zinc in the vapor phase during crystal preparation in accordance with equation (3). In addition, the zinc vacancy because of its double negative charge tends to associate strongly with one of the positively charged donor impurities. This diatomic impurity system will be a singly ionizable acceptor with properties similar to Group IB or VB acceptors. The self-activated blue emission of ZnS has been attributed to this diatomic impurity system. Since the nearest-neighbor pairs formed between the zinc vacancy and the impurity donor are different depending on whether the donor is from Group IIIB or Group VIIB, it was predicted that the self-activated emission spectrum should be different for the two types of donor impurities. The observed difference in peak position is 400 cm^{-1}. This is in accord both as to magnitude and direction with a model of the center in which vacancy and donor are considered to be point charges, -2 and $+1$, in a medium whose static dielectric constant is that of ZnS (*27*). In addition, the dependence of the self-activated emission intensity on sulfur pressure during crystal preparation is in accord with the identification of the activator.

Another emission band involving associated donor-acceptor pairs is observed in ZnS containing equivalent concentrations of Group IB acceptors and Group IIIB donors. This emission is in the red and is attributed to pairs sufficiently closely associated so that radiative transitions may occur between the ground states of the donor and acceptor (*28*). The probability of this transition depends on the overlap of the donor and

acceptor wave functions. Association must not be so close that the states are no longer coulombic. Because of the large central cell correction characteristic of the ground states of donors and acceptors in ZnS, the energies of these states are dependent on the identities of the donor and acceptor. The emission spectrum depends, therefore, on the chemical identities of both activator and coactivator. This is in contrast to the shorter wavelength emission bands which depend only on the chemical identity of the activator. These emission bands involve transitions from the conduction band or from excited states of the donor to the ground state of the acceptor in less highly associated pairs. The transitions for the long and short wavelength emission bands are shown in Figure 14. A typical

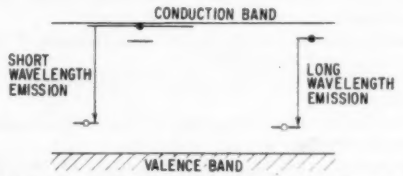

Figure 14. Band theory model for short and long wavelength luminescent centers in IIB-VIB compounds containing donor-acceptor pairs.

emission spectrum showing the two bands is shown in Figure 15. The dependence of the relative intensities of these two emission bands on temperature and impurity concentration is consistent with the identifications. Finally, the difference in transition energy for the two types of transitions is in accord with the donor depths determined from electron trapping phenomena (*29*).

The electronic energy levels of the donor-acceptor pair have been investigated theoretically in a way similar to the Heitler-London treatment of the hydrogen molecule (*30*). The interparticle distances of a donor-acceptor pair are shown in Figure 16. In the analysis, the cores are approximated by point charges; the medium, by a continuous dielectric; and the two particle wave function, by a single product of the separated donor and acceptor wave functions.

$$\psi(-,+) = \psi_D(-)\psi_A(+) \qquad (6)$$

The permuted product is not included because the electron and hole are distinguishable particles. By applying the Hamiltonian, including all the interparticle interactions indicated in Figure 16, to the wave function, it is found that the transition energies involved in absorption or emission between particular donor and acceptor states increase as a consequence of association. In addition, the interparticle interactions are different for absorption than for emission because the lattice modes are polarized differently immediately following optical creation of an electron-hole pair and following their optical annihilation. In other words, for crystals with some polar character, a Stokes shift is predicted even in the continuous dielectric approximation. If the period of orbital motion of the hole and electron becomes long compared to the period of the lattice modes, then the Stokes shift vanishes. The application of the theory to ZnS containing Group IB acceptors and Group IIIB donors tends to support the identification of the red emission as involving transitions between the ground states of donor and acceptor in quite highly associated pairs.

There exists a number of unsolved problems pertaining to the impurities and imperfections responsible for luminescence in covalent crystals. The question of

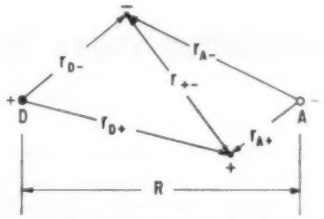

Figure 16. Interparticle distances for associated donor-acceptor pairs.

compensation of impurities by vacancies or by interstitials needs to be resolved experimentally. The impurities or imperfections responsible for edge emission and for the blue emission band of copper need to be identified unambiguously. The outstanding theoretical problem is a quantitative method for taking account of the large central cell correction which exists for donors and acceptors in large band gap semiconductors. There are, of course, many problems associated with non-photoluminescent excitation and energy transfer which are outside the scope of this review.

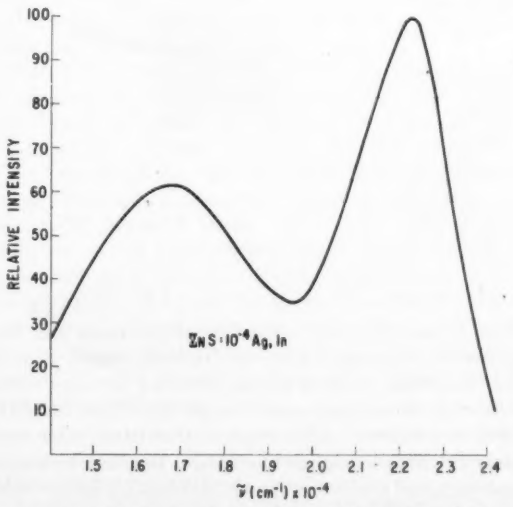

Figure 15. Emission spectrum of cubic ZnS : 10^{-4} Ag, In at 25°C (Apple and Williams).

Conclusions

The nature of the chemical impurities and crystalline imperfections which dominate the luminescence of inorganic crystals is becoming increasingly better understood. For example, the broad bell-shaped absorption and emission bands and the Stokes shift between absorption and emission are quite general properties with the same qualitative origin in all phosphors. The contribution of chemical studies to fundamental research programs on luminescence has increased as more complex phosphors have been investigated. The understanding of covalent luminescent crystals has advanced largely from the impact of

semiconductor theory as modified to large band gap polar crystals. Luminescence involves impurities and imperfections of diverse atomic and molecular types whose characteristics depend on the chemical potential for electrons of the crystal as well as on the structure of the activator system.

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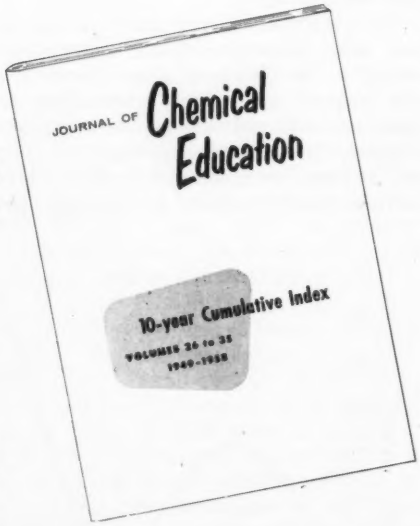

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The Undergraduate Training of Chemistry Majors

A report of the Bucknell Conference[1]

The accelerating growth of chemical knowledge, which has been recognized as an exponential function (*1*), and the improvement (both acknowledged and anticipated) of the secondary school chemistry course have made imperative a re-examination of the traditional program for the training of chemistry majors. The Division of Chemical Education of the American Chemical Society requested Bucknell University to hold a conference during the summer of 1960 to consider the total undergraduate chemistry curriculum. The objectives of the conference were the promotion of a fruitful exchange of ideas among persons interested in and involved in experimental curricula of various sorts, and the stimulation of interest in the modernization of the undergraduate programs at colleges throughout the country.

The conference included 45 college and university men of diverse interests from institutions of diverse purposes. The conference divided into four working groups to consider the problem of up-dating the undergraduate chemistry curriculum. The approaches of these four groups were quite different and their reports show different emphases.[2] No one was brave enough to say that he had discovered the ideal chemistry curriculum, a conclusion that has been reached by others (*2*). However, numerous suggestions for practical programs were put forward, some of which had features common to curricula described in THIS JOURNAL in recent years. Those papers included descriptions of particular curricula now in operation (*3*), discussion of novel or unique treatment of the traditional subject matter areas (*4*), and symposia devoted to instruction in inorganic (*5*) and analytical (*6*) chemistry.

During the last two days of the conference, the original groups were dissolved and new groups were formed according to the subject matter interest of the members. Some thoughts of these groups are also reported here.

The reports of the various groups were presented at plenary sessions of the conference for discussion and cross fertilization of ideas. The conference took no action on any of these reports, so it is not possible to summarize the results in a series of resolutions or conclusions approved by the conference as a whole. However, several ideas appeared so frequently that it seems fair to conclude that they are endorsed by a majority, if not all, of those present. Other ideas are endorsed by fewer in the conference.

[1] June 12–18, 1960. Financial support was provided by the National Science Foundation.

[2] A copy of the complete report may be obtained from Professor B. R. Willeford, Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania.

Opinions Expressed

Impact of improved high school courses. There has recently been an improvement in the quality of high school chemistry as more and more teachers take advantage of the programs supported by the National Science Foundation. The more widespread use of the materials developed by the Chemical Bond Approach and the Chemical Education Materials Study groups will provide more entering undergraduates with excellent backgrounds in chemistry. Similar programs in mathematics will bring about an increase in the number of students who enter college with introductory calculus or who will be prepared to study calculus in the freshman year. The undergraduate college must be prepared to take advantage of this improved high school training as only too few schools have done in the past.

"Trickle-down." The ideas, theories, and experiments on the frontiers of chemistry must be brought from the research laboratory through the graduate program and eventually to the undergraduate program. This movement of advanced material to undergraduate courses (called "trickle-down," a term coined by Peter Yankwich) should be accelerated if students are to be better chemists than their mentors. The "trickle-down" of physical chemistry to general chemistry is recognizable but in other courses the rate of infiltration has generally been slow. Occasionally we may need a revolution rather than an evolution in course content.

"Constant volume." Most undergraduate programs must be formulated within a "constant volume" of about 40 semesters hours devoted to instruction in chemistry. There is no general feeling that this should be expanded at the expense of humanities, social studies, English, or language requirements. The "constant volume" situation indicates a solution in which an increasing emphasis is placed on chemical principles at the beginning, needless repetition is avoided throughout the curriculum, and a realistic recognition of good teaching in high school is mandatory. Perhaps the best hope of increasing the size of the "constant volume" is in better use of high school chemistry.

Utilizing summer time. The size of the "constant volume" in which the undergraduate program operates can also be increased by utilizing the summer periods for assigned readings, independent study, or research. The NSF Summer Programs for undergraduates already in operation encourage more use of this available time.

Content of first course? There was no general agreement as to what constitutes the best freshman course. The majority favored a modernized general chemistry course but a few schools now find it best to begin with

organic chemistry or an integrated chemistry-physics course.

Rescue inorganic. Inorganic chemistry, as distinguished from general chemistry given as a first course, has almost disappeared from the undergraduate curriculum. This situation has resulted partly from the gradual "trickling down" of physical chemical principles into the general chemistry course, which formerly consisted mostly of inorganic chemistry. The belief that inorganic reactions were essentially direct and simple and depended little on structure and mechanism also led to the de-emphasis of inorganic chemistry. Finally, the treatment of inorganic chemistry as an encyclopedic description of the chemistry of element after element and compound after compound has discouraged many teachers and students from cultivating this discipline. Today, however, when new and powerful experimental tools for investigating the structure of inorganic compounds and the mechanisms of inorganic reactions have become available, inorganic chemistry again has become an exciting science and is claiming more and more time of the research scientist. Add to this consideration the great benefit which chemists in other fields would gain from a systematic knowledge of inorganic chemistry, and one is forced to conclude that this important discipline cannot be left out of the undergraduate curriculum. Thus, in addition to the descriptive inorganic chemistry covered in other courses, a modern inorganic course to follow the introductory physical chemistry course is considered essential.

Quantitative techniques and quantitative thinking. Modern chemistry is increasingly quantitative in nature, as all sciences must be as they mature. All undergraduate chemistry courses, not just those in analytical chemistry, should stress the quantitative nature of chemistry and emphasize quantitative procedures in laboratory work. Much of the material of the traditional introductory course in analytical chemistry can be incorporated into other courses. The fear of the professional analytical chemist is that transfer of responsibility for this activity to inorganic, organic, and physical chemists may not be accompanied by the attitude, respect, and demands on exactness that the professional analyst brings to this activity. If such a change is to be made, the instructors in charge of all courses will have to assume a responsibility for "quantitative" chemistry.

Save analytical. Analytical chemistry itself is too important to be eliminated from the curriculum. Though other courses can be used to teach quantitative procedures and principles, it was felt that a course in analytical chemistry with laboratory, probably in the junior or senior year, is needed to give the student appreciation of the exacting work of analytical chemistry.

Physical chemistry→chemical physics. The physical chemistry course should emphasize chemical physics more than has been the general pattern in the past. This trend is indicated in the following parts of a curriculum proposed during the conference (it may be appropriate very soon): Half the first year course is devoted to topics described as chemostatics and ion dynamics. Chemostatics—matter without chemical change—includes the study of particles and properties, states of matter (using a kinetic theory approach to the interplay of forces), introduction of effusion, and the Boltzmann distribution using moderately detailed derivations. Ion dynamics includes equilibria and properties of ionic solutions approached from the side of solutions of ionic crystals, acid ionization from solution of covalent hydroxy compounds, and complex ion equilibriá from development of ion reactions in solution—in all cases using a kinetic approach.

A second year course called "energetics" is given over to the following subject matter: thermodynamics, phase equilibria, solution equilibria, all electrochemical phenomena, crystal structure (including X-ray diffraction), radius ratios, Born-Haber cycles and specific heats (the last is to be treated as an introduction to models used in chemical physics), and diatomic molecule properties, including optical transitions.

A semester course called "chemical physics" would be offered with the following topics: introductory quantum mechanics, with a fairly complete development for the H atom and a modest treatment of H_2^+; bonding theories and their relation to diatomic molecules; electronic structure of solids; electrical and magnetic properties of molecules.

Finally, the subject of chemical physics could be topped off by a course in thermodynamics from a statistical mechanics viewpoint.

New look for organic. In organic chemistry, the increased importance of mechanisms, structural studies, stereochemistry, and such topics requires decreased emphasis on descriptive organic chemistry. The ideal organic laboratory course should attempt to be quantitative. This does not mean that the work now done in quantitative analysis should be transferred to the organic laboratory nor that the precision demanded in the analytical laboratory should be expected in the organic laboratory. It does mean that the tools, techniques, and attitudes of modern analysis should enter significantly into the first laboratory experience in organic chemistry.

Laboratory should be "research." All laboratory courses should emphasize the problem or research approach as much as possible. A student should be given an opportunity to formulate his problem, design an attack, evaluate his experimental results, and draw his own conclusions. A few notable attempts in this direction for the beginning student have been described (*7, 8*) and one laboratory manual has been published with this purpose uppermost (*9*).

Undergraduate research problems. Independent study and research at the senior level are highly desirable aspects of an undergraduate's training (*10, 11*). There was disagreement on whether this should be available to all or limited to honors students.

No "sheep and goats." There seemed to be no inclination among the conference members to distinguish between the undergraduate training for a chemistry major who intends to undertake graduate work and those who terminate their formal training at the bachelor's level. There seemed to be general agreement that what is good training for the graduate schools is also good training for industry (*12*).

No "left nostril" specialists. The recent tendency to break down the boundaries between the traditional areas of chemistry in order to teach without loyalty to one area is a step in the right direction (*13*).

Rates and mechanisms. The importance of rates (*14, 15*) and mechanisms of chemical reactions must be

given a more prominent role in the entire curriculum. The organic course has become immersed with this kind of enterprise but a unified treatment for all of chemistry makes more sense.

Competent Enthusiastic Teaching Produces Results

Finally, it was generally recognized that the teacher is far more important than the curriculum in the instruction of a student. If the chemistry teacher is competent and enthusiastic, and has initiative, almost any curriculum can be utilized effectively. Though certain guide lines can be laid down for a curriculum, the flavor will be determined by the teacher and not by the name given to the course.

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and **W. T. Lippincott**
University of Florida

The College Chemistry Course for Non-Science Majors

A report of the Montana State Conference[1]

The conference on chemistry for non-science majors was sponsored by the NSF and the Division of Chemical Education. Participants in the conference included 28 college teachers of chemistry and five distinguished scholars from other disciplines. The chemistry teachers, selected because of their contributions to chemical education, represented colleges and universities of all sizes and types from all parts of the nation.

The principal purpose of the conference was to examine critically, on an exploratory basis, the course content and method of teaching the chemistry courses for non-science majors and to recommend ways in which such courses can be made more valuable to the thousands of students who are concerned with and vitally affected by the implications of chemistry. The conference has prepared a full report. Copies are available from the office of the Department of Chemistry, Montana State College, Bozeman, Montana.

The program of the conference, in 17 sessions, included a series of lectures by prominent scholars from disciplines other than chemistry, on topics which contained auxiliary material for a terminal course. There also was a series of panel discussions on various phases of the problem of providing and developing a chemistry program for the non-science major. Each lecture or panel discussion was followed by a group discussion.

[1] July 17–23, 1960. Financial support was provided by the National Science Foundation.

The Lectures

A. B. Garrett (Ohio State), "How Can the Most Dramatic Subject Matter of the Whole Academic Curriculum Best Be Taught and Caught?"

Paul Sears (Yale), "What the Field of Conservation Has to Offer a One Course in Chemistry."

Paul Abersold (AEC), "What the Field of Nuclear Science Has to Offer a One Course in Chemistry."

Chauncey Leake (Ohio State), "The Impact of Science on Society" and "Dimensions and Nursery Rhymes."

Joseph Schwab (Chicago), "If I Were to Teach a One Course in Chemistry—Philosophy of Science."

Bentley Glass (Johns Hopkins), "What Non-Science Students Should Know About Chemistry in Order to Understand Biological Phenomena Which Are of Everyday Importance" and "The Research Type of Problem for the Laboratory."

Frank Fornoff (Educational Testing Services), "Testing."

The Panel Topics

Demonstration Problems and Laboratory Problems
Objectives and Syllabi
Great Literature
The Discovery Process: Creativity
Fringe Benefits that May Be Main Benefits
Testing

Highlights of the Lectures

A. B. Garrett presented both a challenge and a charge, suggesting that the unique objective of this course should be achievement on the part of students of the complete cycle: Interest, Understanding, Retention, Applications, Motivation, Continuing Mastery, and back to Interest. He charged the conference to

find the approach and the content for a *modern* chemistry course to do this.

Paul Sears discussed problems of natural resources, emphasizing the interplay among the available resources, the population pressure, and cultural patterns of the society. He suggested that in most of the world today population pressure and prevailing cultural patterns are unfavorable to satisfactory conservation of natural resources. A more responsible attitude toward natural resources will result only from a better appreciation of the laws of science by American youth.

Paul Abersold emphasized the advances in all fields of science made possible by radioisotopes. He demonstrated clearly the importance of including some aspects of nuclear science in the chemistry program and he provided AEC source material for doing this.

Chauncey Leake traced the cultural position of science (and chemistry) against a socio-historical background from the time of the early Greeks and their realization of individual satisfactions and social welfare, through the development of the concept of interpersonal relations and ethics to the development of logic and scientific knowledge. In his second talk, he presented a history of certain chemical concepts as developed by experimental biologists and physiologists. His third talk centered on the evolution and significance of units and dimensions.

Joseph Schwab developed the notion that the current false image of science has created not only suspicion of science but also many unimaginative, unproductive scientists. This false image is of science as a body of absolute truth rather than of fluid enquiry.

Bentley Glass emphasized that the sciences must inescapably become the core of a liberal education. He asked chemistry teachers to attempt to give the student a lasting understanding of what a scientist does, how he carries out his work, and why his method of investigation gives more assurance about the facts of nature than any other approach; to develop the evolution of ideas and their correction using the history of science; and to prepare the "right kind" of teachers.

Summaries of panel discussions:

Demonstration Problems and Laboratory Problems. Convey the research point of view from the very beginning of the course; explore the use of television and films in chemistry teaching; examine the literature of education for techniques for more effective teaching; try some special qualitative analysis techniques.

Hubert N. Alyea dramatically proved the importance and utility of the demonstration technique for developing critical judgment in students.

His conviction is that curiosity, knowledge, and critical judgment should be developed by devoting about 20%, 30%, and 50% of the time, respectively, to each in the terminal course. This would contrast with 20%, 60%, and 20% respectively, in the typical introductory course for chemists.

Great Literature and the Discovery Process. Since any approach to chemistry must inculcate a notion of the dynamic nature of chemistry, the introduction of historical sequence seems most appropriate.

Three techniques of the "historical approach" are to put the student vicariously into the state of knowledge that existed in a past time, to simply require the student to read about the past, and to use biographical or chemical anecdotes in presenting material. The historical approach is but one tool which the chemistry teacher may use in developing this course.

The creative role of problem recognition is important and must not be replaced merely by problem solving.

Fringe Benefits of an Ideal Chemistry Course for Non-Science Majors include an introduction to critical thinking, an understanding of the role of chemistry in the American economy, and insight into the impact of chemistry on world affairs.

Testing. Frank Fornoff listed the objectives of a test and compared essay and objective tests. He discussed test planning and techniques for measuring skills, attitudes, and motivation.

Conclusions

Character of the Course. The character of the chemistry course for non-science majors should be rigorous, with every effort made to limit the number of items covered so that those included can be studied intensively. The course should be no less demanding intellectually than the traditional course in chemistry. It must be organized and taught in such a manner that a student will develop curiosity, will acquire a reasonable amount of chemical information, and will be required to exercise critical judgment.

The student should gain an appreciation of the dynamic and evolutionary character of science as well as its interaction with other cultural forces. He should gain an understanding of the indispensability and limitations of observations, the utility of correlations and classifications, and the tentative nature of theories and postulates; but he should appreciate the great power of discovery that rests in their coordinated use. Experience in the experimental methods of science is indispensable; students should plan, execute, and interpret laboratory experiments.

General Guide for Development of the Course. Preferably, this course should be a one-year course. The subject matter may be selected from many areas.

In making the course intellectually challenging, the instructor should stress the evolutionary development of chemistry, treating in depth a few theories or concepts; he should use mathematics as a tool in quantitative reasoning and as an important means of communication; and he should use an "experimental approach" to the lecture and laboratory programs. Outside reading in chemistry and in the cultural and philosophic aspects of science should be required.

The laboratory should emphasize the "discovery" aspect and provide experience in designing and interpreting experiments. The approach to the laboratory is more important than the coverage.

It is recommended that one or more follow-up conferences or institutes be held for further study and to work out material (possibly with syllabi) on two basic problems:

The research type of laboratory problems that can be developed for the terminal course.

The development in a practical manner of the historical and somewhat anecdotal method, showing the dynamic evolving character of science.

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The Course Content of General Chemistry

The way in which the subject matter or course content of general chemistry has grown during the past several years is cause for concern. For the past few decades the common organization of time has allotted three hours of classroom and three hours of laboratory work each week during one academic year. This has remained true despite the fact that textbooks used for the course have expanded in the number of pages and ideas they contain in an alarming way. Thus, the 1949 edition of one popular textbook contained about 200,000 words; the 1959 edition contains about 260,000. Even more startling, another very well-known general chemistry textbook contained in the 1938 edition about 195,000 words; the 1960 edition contains over 490,000 words!

To determine what college teachers believe *is* the course content of general chemistry, these teachers were approached directly by the use of a questionnaire.

The questionnaire was constructed by listing the items that appeared as index entries in twelve textbooks that are most widely used in college general chemistry courses.[1] This comprised a six-page single-spaced questionnaire consisting of 230 items or topics. The respondents were asked to rate each item according to the scale given in Table 1.

Table 1

Scale rating	Meaning
A	Essential for inclusion in the course
B	Important but do not go into detail
C	Would include when time permits
D	Relatively unimportant, may be safely omitted
E	Unnecessary and should be omitted

This questionnarie was then mailed to the "Director of General Chemistry" in each of 195 colleges together with a covering letter explaining the purpose of the survey. The institutions were selected from a listing in the World Almanac and included representatives of large and small colleges and universities as well as those devoted to liberal arts, engineering, and other professional schools.[2] The response to what was considered quite a formidable questionnaire was far beyond that expected. Of the 195 sent out, 105 were returned carefully completed. Some bore pertinent comments reflecting the way in which the respondents viewed the importance of the survey. Unfortunately it is not possible, since anonymity was preserved, to judge the proportion of the returns which represent the impressions of teachers in the various types of institutions. It is reasonable to hope that the 105 returns were a representative sample of the list of institutions to which mailing was made.

Each item on each questionnaire was then tabulated. An A rating by a respondent gave that item a score of 4; B, 3; C, 2; D, 1; E, 0 on his questionnaire. The score which each item received on all questionnaires was then totaled to give an over-all score. On this basis, the highest possible score for any item would be 420 (that is, it rated A on all 105 questionnaires returned). The values were then scaled proportionally so that the maximum value was 400 and the lowest possible was zero. In this way the score values and their evaluation corresponding to the letter designations in Table 1 are given in Table 2.

Table 2

Score value	Letter value
320–400	A
240–320	B
160–240	C
80–160	D
0– 80	E

Table 3 lists all the items in order of decreasing score. This list of evaluations will reveal some surprises. The purpose here is to present the findings and to leave the interpretation of the information to the reader. There are however, several items that are worth emphasis. For example, only 20 of all of the entries were rated 160 or below—an indication that of the items listed, very few were considered unimportant. No items were rated at 80 or below, which would have corresponded to exclusion from the course. Interestingly, all of the items relating to thermodynamics, free energy, and entropy ranked very low on the list; this is in spite of the fact that the more recent textbooks are tending to include more of this type of material. This may reflect either the pioneering efforts

EDITOR'S NOTE: It should be stated clearly that no interpretation can be made other than that the information here presented reflects the way general chemistry *is* being taught. This in no way can be construed to mean that the course *should* be conducted this way. We are confident, too, that any prospective textbook author who patterns his text closely along the lines suggested in this report may well expect his book to be out of balance a decade hence.

[1] The author will supply interested readers with a list of these books.

[2] The author will supply interested readers with a list of these schools.

of the textbook authors or the reluctance of the users to agree with the trend.

The questionnaire itself was alphabetically arranged, yet there was consistency in the resultant rating of items that were related topically but were widely separated in the order of their appearance in the listing. Thus, *Phase rule* rated 150 and *Phase diagrams* 183, but *Eutectics* rated higher at 206. *Atomic energy* rated 285, the *Atom bomb* 273, and the *Einstein equation of mass-energy equivalence* scored 286. *Partition* scored 197; *Extraction* 195. *Thermochemical equations* rated 253 and *Hess' law* 250, yet *Heat of reaction* scored 342. Curiously, *Quantum numbers* were rated 253 while the *Pauli exclusion principle* was rated lower at 200, but *Atomic structure* had the very high rating of 394 while the *Origin of spectra* scored only 272. This makes one wonder how atomic and molecular structure are actually being taught in the classroom in the light of the way these topics are being treated in the newer textbooks. *Composition of air* rated 353 and the *Atmosphere* 352. Apparently, identification tests for *anions* and for *cations* were considered of about equal importance scoring, 300 and 304, respectively.

Some paradoxes in the ratings may have been due to differing interpretations of the topic title or may imply that some topics are treated qualitatively rather than mathematically. Thus, *Hydrolysis of salts* was rated 383, but the quantitative aspects of hydrolysis, that is, *Degree of hydrolysis* and *Hydrolysis constant* were rated only 298 and 291, respectively. The *Gas laws* scored 395, but *Van der Waals' equation* only 191. Similarly, *Colligative properties* was rated 346 while *Raoult's law* was only 298. The *Electromotive series* was rated 388 but *Oxidation potentials* only 322 and the *Hydrogen electrode* even lower at 272. *Chemical bonding* scored 390 but *General isomerism* only 268. Also, whereas *Ionic equilibrium* was rated at 384, *Common ion effect* scored only 301. *Concentrations of solutions* was rated at 398, yet *Activities of ions* was only 214 and *Titration* was 344.

Other interesting disclosures were that whereas *Bronsted acids* scored 356 and *Arrhenius' theory* 355, *Lewis acids* scored only 278, and that the highest rated of all topics pertaining to organic chemistry, *Classification of organic compounds*, received a score of only 295. All of the topics pertaining to organic chemistry rated at an average of about 230. This corresponds to an interpretation implying that the subject matter would be included in the course only if time permitted. An average of about 10% of the total page space in general chemistry textbooks is devoted to organic chemistry.

The sequence of topics that come under the heading of descriptive chemistry in order of decreasing score was as expected, i.e., the Chemistry of *Oxygen* (382), *Hydrogen* (381), *Halogens* (376), *Nitrogen* (374), *Sulfur* (371), *Alkali metals* (369), etc.

Table 3. A Listing of Questionnaire Items and Their Scores

400	Periodic system
398	Absolute temperature
398	Ionization of acids
398	Concentrations of solutions
395	Gas laws
394	Atomic structure
394	Conservation of mass
393	Redox equation balancing
392	Units and dimensions
391	Conservation of energy
390	Avogadro's number
390	Chemical bonding
389	Boiling point definition
389	Boyle's law
389	Mass definition
388	Electromotive series
388	Vapor pressure definition
387	Law of mass action
384	Ionic equilibrium
384	Ionization constant
384	Kinetic molecular theory
384	Avogadro's law
384	Reversible reactions
383	Activity series of metals
383	Hydrolysis of salts
382	Oxygen chemistry
382	Charles' law
381	Hydrogen chemistry
379	Acids and bases, general
379	Electrolysis
376	Halogen chemistry
376	Law of definite proportions
374	Nitrogen chemistry
373	Equilibrium constant
372	Common ion effect
372	Faraday's law
371	Sulfur chemistry
370	Anhydrides, acid and basic
369	Alkali metals chemistry
369	Equivalent weights
368	Law of combining volumes
368	Nomenclature, inorganic
367	Atomic weight determinations
366	Electrolytic conduction
364	Electricity from reactions
363	Nitric acid and *N* oxides
361	Le Chatelier's principle
359	Ammonia
358	Inorganic carbon chemistry
358	Scientific method
356	Bronsted acid, definition
355	Arrhenius' theory
354	Dalton's atomic theory
353	Composition of air
353	Types of reaction
352	Atmosphere
352	Alkaline earth metals
349	Hydration of ions
348	Catalysis
348	Electrical conductivity
346	Colligative properties
346	Iron chemistry
344	Complex ions
344	Titration
343	Electrode potentials
342	Heat of reactions
340	Ion-electron method
340	Dalton's law
337	Coulomb's law
335	Aluminum chemistry
335	Radioactivity
332	Atomic radii
332	Bronsted theory
330	Phosphorus chemistry
330	Law of multiple proportions
328	Electronegativity
327	Halogen oxyacids
326	Allotropy
326	Buffer solutions
326	Inert gases
326	Magnesium chemistry
325	Cathode rays
322	Types of cells
322	Electron affinity
322	Hydrogen bond
322	Oxidation potentials
320	Alloys
320	Graham's law
318	Moseley's work
314	Reaction rates
314	Ionization potentials
313	Galvanic action
312	X-rays
310	Air, fractional distillation
310	Hydrogen peroxide chemistry
310	Copper and silver chemistry
310	Nuclear energy
308	Brownian motion
306	Zinc chemistry
305	Half-life period
304	Dipoles
304	Cation identification tests
304	Henry's law
303	Silicon chemistry
301	Common ion effect
300	Anion identification tests
298	Crystal structure
298	Hydrides
298	Hydrolysis, degree of
298	Law of Dulong and Petit
298	Raoult's law
297	Rutherford's experiment
296	Metallurgy
296	Water hardness
295	Classifications of organics
294	Flame tests
294	Boron chemistry
294	Van der Waals' forces
292	As, Sb, and Bi chemistry
292	Metallic conduction
291	Hydrolysis constant
290	Cation analytic separation
290	Osmotic pressure
289	Mercury chemistry
289	Lead chemistry
288	Isomerism, organic
286	Chromium chemistry
286	Manganese chemistry
286	Einstein equation
286	Chain reactions
285	Fusion and atomic energy
284	Tin chemistry
280	Mass spectrograph
279	Cobalt and nickel chemistry
278	Lewis acids, definition
275	Activation energy
273	Adsorption
273	Atomic bomb
272	Hydrogen electrode
272	Spectra, origin
271	Dipole moments of molecules
268	Isomerism, general
266	Critical constants
266	Reaction kinetics
265	History of chemistry
262	Nomenclature, organic
258	Cadmium chemistry
258	Mass defect
257	Coordination theory
253	Humidity
253	Law of van't Hoff
253	Quantum numbers
253	Thermochemical equations
252	Organic class reactions
252	Gold chemistry
250	Hess' law
249	Alums
248	Calorimetry
248	Fractional distillation
247	Corrosion
246	Beryllium chemistry
244	Hydrocarbon cracking
242	Subatomic particle accelerators
242	Crookes tubes
240	Photosynthesis
234	Cycles in nature
230	Oil drop experiment
230	Packing fraction
229	Platinum metals chemistry
229	Distillation liquid mixtures
228	Flotation
227	Goldschmidt
227	Poymers
227	Resonance
226	Carbohydrates
224	Magnetism and structure
222	Radioactive dating
222	Constant boiling mixtures
221	Isomorphism
220	Tracer techniques
218	Decomposition potential
218	Photochemistry
217	Proteins
217	Refrigeran gases
216	Germanium chemistry
214	Activities of ions
214	Ion exchange resins
206	Eutectis
204	Cannizzaro's method
203	Detergents
203	Photoelectric effect
201	Rare earths chemistry
200	Equivalent conductance
200	Pauli exclusion principle
197	Partition
195	Extraction and partition
193	Stereochemistry
191	Van der Waals' equation
188	Bragg's law
187	Maxwell distribution law
184	Activity coefficient
184	Antibiotics
183	Dew point
183	Phase diagrams
182	Photography chemistry
180	Ostwald dilution law
176	Biographies of chemists
176	Electron diffraction
175	Cellulose products
166	Mineral names
154	K-electron capture
150	Phase rule
149	Age of minerals
149	Biochemistry
148	Lanthanide contraction
144	Acheson process
140	Optical activity
137	Aromaticity
135	Air conditioning
133	Meson theory
131	Case hardening
125	Free energy
124	Cloud chamber
124	Chemotherapy
124	Enantiotropy
124	Thermodynamics
117	Fajan's rules
116	Entropy
95	Dyes

Total and Static Thermodynamic Properties

Old gas dynamic properties which may be new to the chemist

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This paper has two objectives: To introduce to chemistry students and their instructors some thermodynamic ideas which are usually not presented in chemistry curriculums, suggesting that they have enough philosophical and practical significance so that their inclusion in courses in physical chemistry and thermodynamics is justified from the pedagogical standpoint; and to point out that familiarity with these ideas is of value to the chemist. It can help him communicate with others who are familar with these concepts and who use them. It may suggest new techniques for studying thermodynamic and kinetic problems in which flowing gas streams are used as the tools.

Traditionally, courses in chemical thermodynamics and physical chemistry are concerned with static systems, i.e. systems that are at rest with respect to the observer. I would like to suggest in this paper, however, that a study of gaseous thermodynamic systems is not complete or even adequate unless it includes some elements of gas dynamics. Many chemists, even those with advanced degrees, are unaware that there is a branch of thermodynamics that deals with gases in motion, and that the physical laws and mathematical expressions used to describe it are no less exact and orderly than those of traditional chemical thermodynamics.

Many textbook authors in emphasizing important points go so far as to make statements which, while they are certainly true, practically preclude the possibility that a student will discover, even accidently, gas dynamics. Two ideas frequently found in textbooks may be cited as examples:

Isentropic processes must take place infinitely slowly. They never occur in rapidly changing systems.

The internal energy and heat content (enthalpy) of an ideal gas depend only on the temperature in the absence of gravitational fields, etc.

There is no argument with the validity of the first statement. Nevertheless, it might be criticized. It creates in the student mind the impression that very nearly isentropic processes have significance only in the imaginary situations created by the chemist as an aid to computations. "*Almost* infinitely slowly," in many situations, however, might mean "quite rapidly." Real systems, e.g. gases flowing at high velocities in pipes, frequently undergo *almost* isentropic changes involving very large pressure and temperature changes in times of the order of milliseconds.

The second statement is true by definition. Implicit in most formulations of this statement is the idea that by internal energy is meant all the energy of the substance above that amount that it contains at some arbitrary temperature. The total amount of such energy that a gas contains (which may include energy of motion of the gas as a whole) is usually ignored. Moreover, the probability that the student may examine the consequences of the gas being in motion is minimized. He is not even told that the equations he is about to study apply only to a gas at rest and to some of the properties of a gas in motion.

Presented before the Division of Chemical Education at the meeting of the ACS, April, 1960, Cleveland, Ohio.

Total and Static Temperature and Pressure

Temperature and Mach Number. Physical chemistry texts traditionally cite two conditions that must be met if a gas is to be considered an ideal gas. It must be described by the equation $pV = nRT$, and the internal energy and enthalpy must depend only on the temperature. The second assumption implies that the gas may not be in motion, for if it were in motion, our definition of temperature would be ambiguous.

Consider, for example, a well insulated box containing one mole of an ideal monatomic gas at rest. The box also contains a thermometer. By our second condition for describing a perfect gas, the kinetic energy of the atoms in the box is $^1/_2Nmc^2 = {}^3/_2RT$. (Traditional notation is being used here.) The enthalpy is $E + PV = {}^5/_2RT$. Let the box containing the gas now be slowly accelerated to some velocity, for example c, the root mean square velocity of the atoms in the box. The thermometer will register no change in temperature, inasmuch as there was no mechanism by which heat could be transferred through the walls of the box. But the atoms in the box now have associated with them twice the kinetic energy they had when the box was standing still, and, by definition, 1.6 times the enthalpy (pV has not changed, of course). We are now faced with the problem of describing the temperature of the gas in the box. Is it T, $2T$, or $1.6T$? The answer is that the gas can be characterized by reference to several temperatures.

If the gas is flowing through an adiabatic pipe in which the only work involved is that of the gas working to change its own velocity, two temperatures are sufficient. These temperatures are:

The temperature that the molecules of gas themselves feel, called the *static temperature*. This is the temperature that determines all the properties that are usually associated with temperature, e.g. the rates of chemical reactions, vapor pressures of solid or liquid particles entrained in the stream, etc. It is also the temperature that is used with the static pressure (to be described below) in the equation of state.

The temperature that the molecules would feel if the gas were adiabatically brought to rest, called the total, or *stagnation*

temperature. The total temperature, being a measure of all of the energy associated with a given mass of gas, above some arbitrary reference state having a (defined) energy of zero, is the property that is conserved as a gas flows through an adiabatic pipe, regardless of how variations of the pipe's geometry may change the velocity of the gas and consequently its static temperature.

The relationship between the static and total temperature is very easily derived from a consideration of the conservation of energy. Consider a gas flowing through an adiabatic pipe. If the pipe has a variable cross sectional area, the velocity of the gas in the pipe will change as it moves from point to point in the pipe. However, when the gas speeds up, the static temperature must go down, because the pipe is adiabatic and any increase in kinetic energy of the volume element of the gas must be at the expense of the chaotic kinetic energy of the individual molecules. (This example differs from the previous example in that the gas itself is supplying the work of expansion necessary to accelerate itself.) We are in this case concerned with changes in $E + pV = H$. This relationship can be expressed by the equation

$$\tfrac{1}{2}mv_1^2 + mh_1 = \tfrac{1}{2}mv_2^2 + mh_2$$

where m is the mass of gas in a given volume element, the v's are the velocities of the gas at observation stations 1 and 2, and the h's are the specific enthalpies, $\int_0^T c_p\,dT$. The first term on each side of this equation is the kinetic energy associated with a packet of gas of mass m moving as a whole; the second term is the thermal energy the gas has by virtue of the fact that it is at some temperature above absolute zero. The sum of these two terms is thus all of its energy (insofar as we are in this case concerning ourselves only with these two kinds of energy) and is called the total enthalpy of the gas. Since m appears in all the terms of this equation, it may be cancelled out and

$$\frac{v_1^2 - v_2^2}{2} = h_2 - h_1 = h \qquad (1)$$

where Δh is the change of enthalpy undergone by unit mass of the gas in moving from station 1 to 2 in the pipe. If c_p, the specific heat of the gas, is assumed constant over the temperature range covered from station 1 to station 2,

$$\Delta h = \int_{T_1}^{T_2} c_p\,dT = c_p\,(T_2 - T_1)$$

Substitution of this expression for Δh into equation (1) yields:

$$v_1^2 - v_2^2 = 2c_p(T_2 - T_1) \qquad (2)$$

Equation (2) relates the velocity and temperature of the gas in any section of an adiabatic pipe to the velocity and temperature in any other section.

Equation (2) permits us to relate the total or stagnation temperature to the static temperature and velocity of the gas. Let us now slow down the gas at station 1. This can be done, if flow is subsonic, merely by enlarging the pipe at station 1. If the flow is supersonic, it is necessary to generate a shock wave in the stream to slow it down and then let it flow into the enlarged section. This process can be adiabatic, but it is not isentropic. If v_1 is made very small compared with v_2, it can be neglected. T_1 becomes the total temperature, T_T, and equation 2 becomes

$$v_2^2 = 2c_p(T_T - T_2) \qquad (3)$$

where v_2 and T_2 are the velocity and temperature at station 2. Equation (3) can be written

$$T_T = T_2\left(1 + \frac{v_2^2}{2c_pT_2}\right) \qquad (4)$$

Equation (4) gives the total temperature explicitly as a function of the velocity, static temperature, and specific heat of the gas. Since T_T is a conserved property of the system, it can be used to calculate the relationship between temperature and velocity in any other part of the system. In this case, when $v_2^2 = c^2 = 3RT_2/Nm$ and $c_p = \frac{5}{2}R$, the term $v_2^2/2\,c_p\,T_2$ becomes 0.6 and $T_T = 1.6\,T_2$.

Gas dynamicists usually take equation (4) one step further to non-dimensionalize it and thus make it completely independent of the units that are used to express the variables. It will be recognized that $c_p\,T_2 = a_2^2/(\gamma - 1)$ where a_2 is the speed of sound in the gas at station 2 and γ is the ratio of the heat capacities c_p/c_v. Equation (4) then becomes

$$T_T = T_2\left(1 + \frac{v_2^2(\gamma - 1)}{2a^2}\right)$$
$$\frac{T_T}{T_2} = \left(1 + \frac{\gamma - 1}{2}M_2^2\right) \qquad (5)$$

where $M_2 = v_2/a_2$. M_2 is thus the ratio of the velocity of the gas stream to the speed of sound in the stream at station 2. It is called the *Mach number* at station 2. The Mach number is a very useful parameter. Gases having similar γ's will have similar ratios of many of their variables at similar Mach numbers. For example, helium at a static temperature of 300°K at a Mach number of two will have the same ratio of total to static temperature as helium at a static temperature of 1200°K flowing at a Mach number of two, even though the actual velocity of the helium in the second case will be twice that in the first. Although the speed of sound in hydrogen is greater than four times that in hydrogen chloride at room temperature, their temperature ratios will be similar at similar Mach numbers in spite of the four-fold difference in velocity. Carbon dioxide, water, nitrous oxide, sulfur dioxide, and hydrogen sulfide, form another group of gases that will behave similarly near room temperature. A plot of the ratio T_2/T_T as a function of Mach number is given in the figure for various values of γ. The plot suggests that even for only moderately high Mach number flows, the temperature ratios are appreciable, e.g. air ($\gamma = 1.4$), initially at 500°K would be cooled to room temperature by allowing it to flow through a properly designed pipe where it is accelerated to a Mach number of about 1.8. Air could be cooled from 1000°K to room temperature by allowing it to accelerate to a Mach number of about 3.4. This would require the diameter of the pipe to vary by a factor of only about 2.5. Of course, if it is necessary to slow down the gas so that it may be studied, the temperature will rise again unless some provision has been made to remove heat from it while it is traveling at high velocity.

Pressure. If we consider an adiabatic and isentropic system, the static pressures and static temperatures at any two locations in the pipe must be related

to each other through the expression

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\gamma-1}{\gamma}}$$

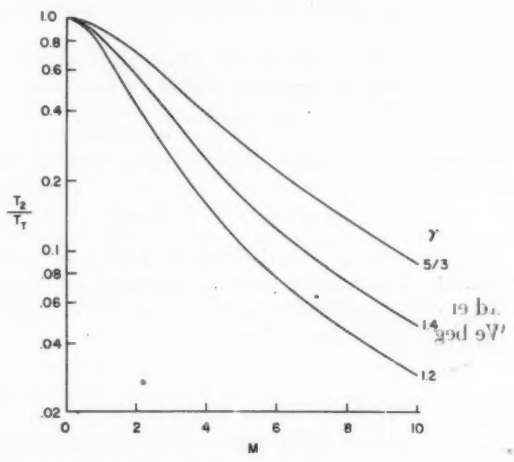
If the gas is at rest at station 1,

$$\frac{T_T}{T_2} = \left(\frac{p_T}{p_2}\right)^{\frac{\gamma-1}{\gamma}} \tag{6}$$

Substitution from equation (6) into equation (5) gives the ratio of the total pressure to the static pressure at any point in the stream in terms of the Mach number.

$$\frac{p_T}{p_2} = \left(1 + \frac{\gamma-1}{2} M_2^2\right)^{\frac{\gamma}{\gamma-1}} \tag{7}$$

Because γ must always lie between 1 and 1.67, $\gamma/(\gamma - 1)$ will always be greater than 1. Thus the pressure ratio, p_T/p_2, will always be greater than the corresponding temperature ratio T_T/T_2.



Variation of static/total temperature ratio with Mach number.

Significance to the Chemist

Aside from any pedagogic value these thermodynamic properties may have, they are useful tools that should not be denied the chemist. They may suggest valuable techniques for sampling high temperature gaseous mixtures or quenching chemical reactions for example.[1] This is a direct result of the fact that both the temperature and pressure change in such a way that chemical reactions are slowed down as the velocity of the gas stream is allowed to increase.

If the rate of a gas phase chemical reaction is given by:

$$\text{rate} \propto p^n e^{-E/RT}$$

where n is the order of the reaction and E is the activation energy,

$$\ln\frac{\text{rate}_T}{\text{rate}_2} = \frac{n\gamma}{\gamma-1}\ln\left(1 + \frac{\gamma-1}{2} M_2\right) + \frac{E}{RT_1}\left(\frac{\gamma-1}{2} M_2^2\right) \tag{8}$$

where the ratio of the rate of a given chemical reaction in a stagnation region (rate_T) to the rate in any other part of the pipe (rate_2) is given by equation (8). The effect that increasing that Mach number of the gas has on gas phase kinetics is shown by the illustration in the table. Here we have tabulated the normalized (to 2000°K) rate of a second order gas phase reaction having an activation energy of about 40 kcal.

Table 1. Variation of Reaction Rate with Mach Number

M	Rate (rate at 2000°K = 1 in static system)
0.0	1.0
0.5	0.43
1.0	0.04
3.0	10^{-11}

The implication of Table 1 is that the rate of this chemical reaction could be lowered by a factor of about 25 merely by permitting the gas to flow through a critical flow orifice, i.e., an orifice small enough that the pressure is reduced by about one half for most gases, and it could be slowed down by a factor of 10^{11} by allowing it to accelerate to a Mach number of 3 through a suitably designed nozzle. Attempts have been made to take advantage of these phenomena in studying the composition of high temperature gases and in conducting chemical syntheses[2] of substances which can ordinarily not be isolated from a reacting mixture while the mixture is being cooled down. Here again, the chemist must use his ingenuity to devise techniques for removing heat from the flowing gas while it is moving at the high velocity so that it will not be heated to too high a temperature when it is finally slowed down.

One word of caution should be injected at this point. The treatment given in this paper is highly simplified. It has been essentially a one-dimensional treatment. It has neglected the effects of some extremely important properties of gaseous systems such as viscosity. It has assumed ideal gas behavior and constant heat capacities. The nature of real systems will perturb the glib conclusions drawn in this paper to some extent, but not too much; they should be considered at least the minimum gas dynamic tools of the well trained chemist.

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[1] For example, the latest of a series of such studies is described by Wegener, Peter P., ARS Journal, **30**, 322 (1960).

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Textbook Errors, 30

The Ionization Constant of Water

The subject of ionic equilibria is treated in three of a student's undergraduate chemistry courses: General, Analytical, and Physical Chemistry. The idea of activity and the use of activity coefficients are often introduced at the same time. Because the type of chemistry covered in these undergraduate courses is largely limited to that in aqueous solutions, a great deal of emphasis is placed on the ionization of water. Many phenomena are treated in the light of this fact. As a result, the student is confronted early in his career with the ionization constant of water. A survey of textbooks shows, however, that in many the treatment of this topic is simplified without the student being made aware of the approximation. While the effect of concentration on the value of the activity coefficient is usually discussed in connection with other ionic equilibria, it is often forgotten or neglected when the ionization of water is considered. As a result some textbooks[1] contain a statement to the effect that the ion product value of water is a constant under all conditions at a given temperature.

The ionization of water can be represented as

$$H_2O \rightarrow H^+ + OH^- \qquad (1)$$

More molecules of water may be involved, depending on the extent of hydration of the ions. Since the degree of this hydration is not known exactly, equation (1) already is an approximation.

The ionization constant expression is then

$$K_w = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} \qquad (2)$$

In pure water a_{H_2O} is unity and in dilute aqueous solutions this term is approximately equal to unity. Consequently, the expression can be simplified to

$$K_w' = a_{H^+} \cdot a_{OH^-} \qquad (3)$$

Most textbooks present equation (3) but in some no attention is called to the fact that this ion product is a constant only in pure water or in very dilute solutions. The correct expression is

$$K_w \cdot a_{H_2O} = a_{H^+} \cdot a_{OH^-} \qquad (4)$$

Practically all textbooks use 1.008×10^{-14} as the value for K_w at 25°C. This was determined by Harned and Hamer (*1*). Only in dilute solutions or in pure water is this equal to the ion product of water. At moderate concentrations the ion product differs significantly from this. Thus, in 1 *M* KOH, $a_{H_2O} = 0.963$ (*2*). The product of the ionic activities is then equal to $1.008 \times 10^{-14} \times 0.963 = 0.971 \times 10^{-14}$. As the concentration of the KOH increases this number becomes smaller.

Under those conditions for which the product of the ionic activities is equal to K_w it follows also that

$$pH + pOH = 14 \qquad (5)$$

For more concentrated solutions, however, the relationship is

$$pH + pOH = 14 - \log a_{H_2O} \qquad (6)$$

Furthermore, if this distinction is kept in mind it is easier to arrive at the correct expression for the standard emf of the hydrogen electrode in alkaline solutions. We begin with the reaction

$$H_2 \rightarrow 2H^+ + 2e \qquad (7)$$

For this reaction at 25°C.,

$$E = 0.02958 \log a_{H_2} - 0.05916 \log a_{H^+} \qquad (8)$$

From equation (2)

$$a_{H^+} = K_w \cdot a_{H_2O} / a_{OH^-} \qquad (9)$$

Substituting this in equation (8) gives

$$E = 0.8282 + 0.05916 \log a_{OH^-} + 0.02958 \log a_{H_2} - 0.05916 \log a_{H_2O} \qquad (10)$$

This is in accord with equation (11) given by Latimer (*3*) for the reaction at the hydrogen electrode in alkaline solutions:

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e \qquad (11)$$

If one uses the assumption that K_w equals the ion product, then the last term in equation (10) drops out of the expression.

Equation (2) can also be written

$$K_w = (m_{H^+} \cdot m_{OH^-})(\gamma_{H^+} \cdot \gamma_{OH^-} / a_{H_2O}) \qquad (12)$$

The term $(\gamma_{H^+} \cdot \gamma_{OH^-} / a_{H_2O})$ has been evaluated under a variety of conditions. It is dependent on the value of the radii of the ions in solution. Even in solutions having an ionic strength less than 0.25 the deviation becomes appreciable (*4*).

It is true that for work in dilute solutions these differences are small, but the student should be made aware of approximations that are made. The treatment of the ion product constant of water thus affords the teacher an excellent opportunity to point out the fact that though the activity of a pure substance is unity, this value changes as contaminants are added.

Suggestions of material suitable for this column, and guest columns suitable for publication directly, are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. To be presented the error must occur in at least two independent standard books.

The author wishes to thank Dr. W. J. Hamer and Dr. K. J. Mysels for their help in the preparation of this material.

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(1) Harned, H. S., and Hamer, W. J., *J. Am. Chem. Soc.*, **55**, 2194 (1933).
(2) Akerlof, G. C., and Bender, P., *J. Am. Chem. Soc.*, **70**, 2366 (1948).
(3) Latimer, Wendell M., "Oxidation Potentials," 2nd ed., Prentice Hall, Englewood Cliffs, N. J., 1952, p. 32.
(4) Harned, H. S., and Owen, B. B., "Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, 1950, p. 488.

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The University of Texas
Austin

A Flexible Undergraduate Chemical Engineering Program

In today's rapidly developing technology the engineer is often faced with problems which bear little resemblance to those considered as a student. Indeed the only reliable "tools" which the student develops during his university career are his knowledge of the fundamentals of science and the techniques of synthesis and optimization. Furthermore, each engineer must be well versed in broad areas of science and mathematics in order to be prepared to meet this challenge. Thus much of the traditional training offered in the standard engineering curricula is losing the importance which was once attached to this phase of engineering education.

The chemical engineering faculty at The University of Texas recognized these trends some years ago and, as a result of a rather intensive study, concluded that the formulation of a curriculum at a state supported university should be governed by several principles. Flexibility was deemed one of the most important features of a good program. The students who matriculate in chemical engineering at Texas (or any state supported school) have widely divergent backgrounds, interests, abilities, and training. It is impossible to design a fixed curriculum which would fit the needs of each student; hence a good program must be flexible enough to permit the individual student to pursue his own interests.

Secondly, there are certain fundamentals which must be rediscovered by each student. It is these fundamentals which comprise the foundation of engineering analysis and as a consequence must be stressed in a well developed program. This portion of the curriculum must be completed by each student and there can be no flexibility in this area.

In addition to the fundamental and technical work, studies in advanced English, the humanities, and social sciences should also be required. These courses provide the basis of the broad education which is required of each practicing engineer. Although the student may be allowed some freedom in selecting the particular non-technical courses to be included in his program, the total number of these courses should be specified.

Finally, it was noted that a good curriculum is one which is being studied and reviewed continuously. The faculty must insure that the prescribed work accomplishes the desirable objectives without duplication or inefficient arrangements. In other words, a curriculum must be a living program which reacts to the new discoveries and developments of science and engineering.

The Required Core Curriculum

The present program at The University of Texas is a combination of required work and electives. The required work or core curriculum consists of 118 semester hours with approximately 50% in mathematics and

Core Curriculum (113 Credits)

Chemical Engineering		
The Crystalline State	2	
Thermodynamics and Ch.E. Calculations	6	
Unit Operations	12	
Design	3	
		23
Chemistry		
Inorganic	8	
Organic	8	
Physical	8	
Quantitative	5	
		29
Drawing		3
Engineering Mechanics		
Statics	2	
Strength of Materials	3	
Dynamics	3	
		8
Electrical Engineering		3
Non-Technical Subjects		
English	12	
Government	6	
History	6	
Elective	3	
		27
Mathematics*		
Analytic Geometry	3	
Calculus	6	
Differential Equations	3	
		12
Physics		8
Total credits:		113

* College Algebra and Trigonometry will be required for admission to the College of Engineering.

Block Courses (21 Credits)

I. Chemical Engineering
- Process Theory
- Process Evaluation
- Advanced Thermodynamics and Kinetics

Mathematics
- Advanced Calculus
- Vector and Tensor Analysis
- Complex Variables
- Fourier Series and LaPlace Transforms

II. Chemical Engineering
- Process Theory
- Advanced Thermodynamics and Kinetics
- Water Treatment Engineering and Corrosion

Mathematics
- Statistics

Chemistry
- Petrochemicals
- Principles of Colloid Chemistry
- Inorganic Chemistry

III. Chemical Engineering
- Advanced Thermodynamics and Kinetics
- Automatic Control
- Basis for Reactions in Solids
- Water Treatment Engineering Corrosion

Mathematics
- Advanced Calculus

Management Engineering
- Industrial Management

IV. Physics
- Atoms and Electrons
- Introduction to Nuclear Physics

Chemical Engineering
- Nuclear Engineering
- Nuclear Fuel Processing

Mathematics.
- Advanced Calculus

Approved elective in Electrical Engineering

V. Chemical Engineering
- Basis for Reactions in Solids
- Micaceous Minerals
- X-Ray Analysis
- Thermochemical Mineralogy

Physics
- Atoms and Electrons

Approved elective in Electrical Engineering

VI. Psychology
- Introduction to Psychology

Management Engineering
- Industrial Management

Business Law

Language

Advanced Economics

Advanced English

VII. Any three courses, Sophomore rank or higher, which are approved by the Departmental Chairman and for which the student has the prerequisite.

science, 30% in engineering and design and 20% in non-technical subjects. A detailed outline of the core curriculum is given in the table. These required courses have been carefully selected to fulfill the requirements set forth in the preceding paragraphs.

There are a number of changes in this listing of courses as compared to the requirements of previous years. Notable changes include the addition of a course dealing with the solid state and one in integrated design. However, the general features of the program are still quite similar to the "standard" chemical engineering curriculum.

It should be emphasized that the undergraduate engineering program at Texas is four years in length and the work has been carefully tailored to fit into this time schedule. To conform to this schedule, algebra and trigonometry will be required for admission to the College of Engineering beginning in 1962 and will no longer be a part of the college-level required work. Equivalent courses will be offered in the high schools.

The Block Electives

The elective program consists of 21 hours to be selected by each student with the approval of his advisor. The option courses are arranged into "blocks" each block having an underlying theme. Generally the student will be required to take 12 semester hours from any one block and 9 semester hours from any other block. This arrangement was devised to prevent the student from "squandering" his available time on a number of diverse topics rather than concentrating his efforts on one or two specific areas. Certainly the student will not attain the status of a specialist in this way, but at least he will achieve some proficiency and understanding in his areas of interest. Some students of unusual capabilities and those students with a definite goal in mind will be permitted to select all 21 hours from one block of courses if desired. Furthermore, there is some freedom in formulating new sequences or blocks of courses to meet the needs of those students with special interests such as bio-engineering, fluid mechanics, communications, reservoir engineering, etc.

The structure of the option program is unique. This system permits a great deal of flexibility on the student's part but still allows the advisor some measure of control. To achieve this flexibility, a number of courses must be deleted from the standard engineering curriculum. Decisions assessing the worth of individual courses must be based on the principles which have been stated in previous paragraphs. However, the faculty at Texas feels that the values which were lost by dropping certain required courses from the curriculum will be more than compensated by the advantages of the option program.

As examples, seven blocks of electives are given in the table. A brief examination of each of these blocks will reveal the theme which they are intended to represent. It should be reiterated that the blocks of courses shown here are suggested listings; other arrangements are possible for students who might have other interests. Another notable feature of the option program is that the courses are not necessarily of technical nature. For example, interested students may elect to study various aspects of industrial management and business procedures. This feature of the option program is emphasized by Block VI.

This curriculum was first offered to chemical engineering students entering the university in the fall of 1960. The chemical engineering faculty feels that this type of program, with increased emphasis on the fundamentals of science and engineering, is geared to educate engineers capable of resolving the problems of modern technology.

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University of Colorado
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A Demonstration of Optical Rotation with an "Eskimo Yo-Yo"

In 1822 A. Fresnel[1] explained optical rotation by representing plane polarized light as a combination of two circularly polarized waves. A rotation of the plane, defined by the components of the left and right circularly polarized waves, occurs when one of the waves is slowed with respect to the other. If one wave is retarded a full wavelength in traveling through an optically active medium of length l, then the plane of linear polarization is rotated π radians. In general, the difference of the number of waves of left and right circular light of wavelengths λ_l and λ_r will be $l[(1/\lambda_l) - (1/\lambda_r)]$, so the left angular rotation of the plane is

$$\alpha = l\pi[(1/\lambda_l) - (1/\lambda_r)]$$

This rotation is often expressed in terms of the refractive indices n_l and n_r for the respective waves. Since the wavelength is inversely proportional to the refractive index and directly proportional to the wavelength *in vacuo*, the rotation is given by

$$\alpha = \frac{l\pi}{\lambda_{vac}}(n_l - n_r)$$

A demonstration of these concepts can be performed with a toy called the "Eskimo yo-yo."[2] It consists of two rubber balls, each attached to one end of a five-foot plastic string. A handle is fixed near the middle of the string. Both balls are swung in opposite directions, and by moving the handle in an up and down motion, the balls can be made to travel a circular path in perfect synchrony (see Figure 1).

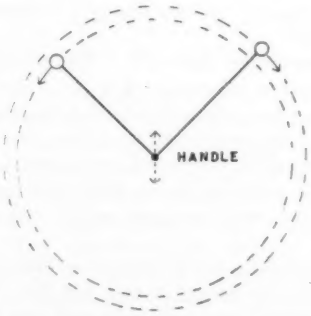

Figure 1. Illustration of "Eskimo yo-yo." Handle is moved up and down to provide synchronous rotation of balls.

The synchronous rotation of the balls illustrates the effect of the two circularly polarized beams of light. The up and down motion of the hand defines the direction of linear polarization. A feeling for this plane is particularly evident from the action of the toy. To represent the forward motion of a beam of plane polarized light, the operator of the yo-yo walks forward so the rotating balls trace two helical paths. The effect of optical rotation may be demonstrated by slowing the rotation of one ball for a moment so that the linear action of the hand is rotated to another angle. This works best going from an up and down motion to a horizontal motion, which corresponds to an optical rotation of 90°. A 45° rotation is shown in Figure 2.

Occasionally the balls collide, particularly during the demonstration of optical rotation. This catastrophe seems to add to the class's enjoyment of the demonstration, mostly by way of the lecturer's plight. It is only fair to say that some practice is needed to operate an "Eskimo yo-yo," but the results seem to be worth the trouble.

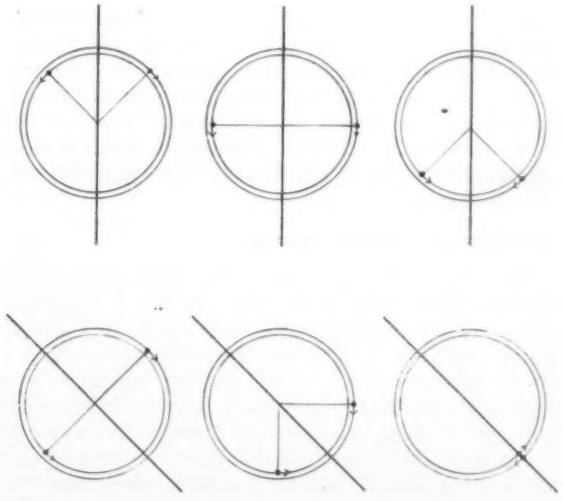

Figure 2. Plane polarized light formed from two in-phase circular components. Circular components are illustrated by rotating balls. Top figures indicate the state of vertical polarization. Bottom figures indicate polarization at −45° and may be obtained from the vertical state when the counterclockwise component undergoes a relative speed-up of 90° with respect to the clockwise component.

[1] Fresnel, A., "Oeuvres completes d'Augustin Fresnel," 1, No. XXVIII, 1822, pp. 731–51; see also Lowry, T. M., "Optical Rotatory Power," Longmans, Green and Co., Inc., New York, 1935, pp. 13–20.

[2] A model called the "Eskimo Go" is manufactured by Creative Capers, Claremont, California.

✦ ✦ ✦

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University of New Mexico
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Apparatus for Oxygen-Sensitive Volumetric Solutions

Volumetric solutions of strong reducing agents are seldom used in analytical laboratory courses because of the difficulty of protecting these reagents from the air. Although several systems for work with oxygen-sensitive volumetric solutions are described in the literature,[1–4] most of these require special equipment and glass-blowing skill beyond that of the student. The apparatus we describe here is for inert atmosphere storage and titration, and is easily constructed from components available in the average college laboratory.

The apparatus was developed to facilitate the preparation, storage, and use of vanadium(II) solutions. It consists of an upward-flow reductor, a storage reservoir and delivery system, and a titration flask. Two modifications of the reservoir-delivery system are described: a gravity-flow (stationary) system, and a pressure-flow (portable) system. All phases of operation, from production of reducing agent to titration, are carried out in an inert atmosphere of gaseous nitrogen.

The Upward-Flow Reductor

The reductor (Fig. 1) consists of a gallon bottle to hold the solution to be reduced, and a 2 cm × 30 cm column packed with 5% amalgamated zinc (20-mesh) held in place by glass wool plugs at top and bottom. The exit tube from the column should be of small outside diameter; usually 4-mm tubing is satisfactory.

After the solution to be reduced is introduced through funnel *A*, *S*-1 is closed and gas pressure applied at *B* with screw clamp *C* open. The screw clamp is then manipulated to adjust the flow rate of solution through the reducing column, *D*.

The Reservoir-Delivery System

The Gravity-Flow Reservoir. The principal parts of the gravity-flow reservoir (Fig. 2) are a stoppered gallon bottle containing a pressure regulator, a second gallon bottle to serve as the reservoir proper, and a 50-ml, side-arm buret. The pressure regulator is a large test tube filled with mercury, in which is immersed a length of tubing extending out through the stopper of the bottle. Mounted in the stopper of the reservoir bottle are a tube, *F*, of large enough inside diameter to admit the exit tube of the reductor; a lead-in, *J*, from the pressure regulator; and a sintered-glass gas bubbler, *G*.

The buret tip was cut off and a thick-walled capillary drawn and bent to make an offset buret tip which is attached by means of a piece of Tygon tubing. The tip therefore enters the titration flask more easily and the buret does not become warm when titrations are run at elevated temperatures.

All rubber tubing connections are made with pressure tubing that has been saturated with paraffin. It is advisable that all stoppers be wired in position.

To fill the reservoir, nitrogen pressure is applied at *E* with screw clamp *F* open, allowing a slow but continuous flow of gas from the reservoir. The exit tube of the reductor is extended into the reservoir through *F*. Gas pressure is then applied at *B* (Fig. 1), forcing the solution to be reduced through the reductor and filling the reservoir with reduced solution. If the solution in the reservoir is not homogeneous, it is stirred by bubbling nitrogen through *G*.

To fill the buret, nitrogen pressure is increased in the reservoir by turning *S*-2 so that the nitrogen passes through *J*. The screw clamps *F* and *K* are closed and *L* is opened. The stopcock of the buret is opened until a siphon is created from the reservoir to the buret. Then the stopcock of the buret is closed and screw clamp *K* is opened. Screw clamp *L* is closed when the buret is filled.

The Pressure-Flow Reservoir. The essential parts of the pressure-flow reservoir (Fig. 3) are the same as those of the gravity-flow reservoir, the principal difference between the two being that the pressure-flow system is mounted on a single buret stand for easy portability. The reservoir is charged, and the content is stirred, in the same manner as for the gravity-flow system.

To fill the buret, *S*-3 is turned to direct the entering nitrogen into the reservoir and not into the pressure regulator; screw clamp *M* is closed and *P* is opened, the buret stopcock is closed, and *S*-4 is closed. When the buret is filled, screw clamp *P* is closed and *S*-3 opened at all three ports. Then *S*-4 is opened, a pressure head of mercury is built up, *S*-3 is rotated 180°, and the nitrogen line may be removed.

The Titration Flask

A 300-ml three-necked flask (Fig. 4) has been found to be the most convenient for electrometric titrations in an inert atmosphere.[2] Inserted into the stopper of one neck is a short piece of glass tubing of sufficient inside diameter to admit the buret tip and serve as a gas exit at the same time. In the stopper of the center neck are a thermometer, a gas-entrance tube, and an

[1] Stone, H. W., and Beeson, C., *Ind. Eng. Chem., Anal. Ed.*, **8**, 188 (1936).
[2] Lingane, J. J., and Pecsok, R. L., *Anal. Chem.*, **20**, 425 (1948).
[3] Stone, H. W., *Anal. Chem.*, **20**, 747 (1948).
[4] McEwen, D. L., and DeVries, T., *Anal. Chem.*, **30**, 1889 (1958).

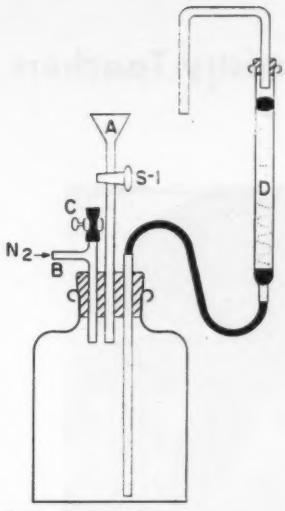

Figure 1. Reductor.

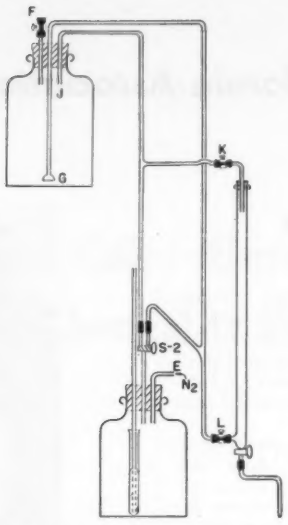

Figure 2. Gravity-flow reservoir.

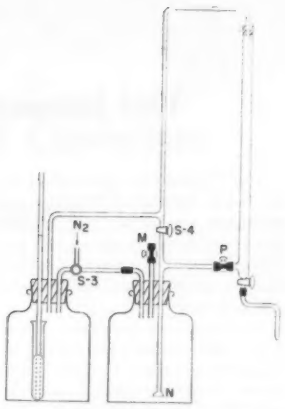

Figure 3. Pressure-flow reservoir.

opening for an indicator electrode. The stopper of the third neck holds one arm of a bridge to a reference electrode. The arms of the bridge are sealed at the ends by sintered-glass disks.

Use of Apparatus with V(II) Solutions

Vanadium(II) is one of the most powerful inorganic reductants available as a volumetric solution. Vanadium(II) is thermodynamically capable of reducing hydrogen ion in acid solution,

$$V^{++} + H^+ = V^{+3} + {}^1/_2H_2;$$

and vanadium(II) and (III) are sensitive to air oxidation.

$$2V^{++} + {}^1/_2O_2 + 2H^+ = 2V^{+3} + H_2O.$$
$$2V^{+3} + {}^1/_2O_2 + H_2O = 2VO^{++} + 2H^+.$$

The stability of a vanadium(II) solution in the gravity-flow reservoir system was studied over a period of several days. Vanadium(II) concentration was determined by titration of a standard permanganate solution. End points were measured electrometrically using a vacuum-tube-voltmeter and platinum-calomel electrodes. The equations for the preparation of vanadium(II) by reduction of a sulfuric acid solution of vanadium(V), and for the three potential-breaks in the titration of potassium permanganate by vanadium-(II) are:

$$2HVO_3 + 3Zn + 5H_2SO_4 = 2VSO_4 + 3ZnSO_4 + 6H_2O$$
$$10VSO_4 + 6KMnO_4 + 6H_2O = 10HVO_3 + 6MnSO_4 + 3K_2SO_4 + H_2SO_4$$
$$VSO_4 + 2HVO_3 + 2H_2SO_4 = 3VOSO_4 + 3H_2O$$
$$VSO_4 + VOSO_4 + H_2SO_4 = V_2(SO_4)_3 + H_2O$$

A solution approximately 0.06 *M* in vanadium(V) was prepared by dissolving ammonium metavanadate in 1 *N* sulfuric acid. The storage-delivery system and the titration flask were flushed out with nitrogen. Tank nitrogen was made oxygen-free and humidified by passing it through a continuously regenerated vanadous sulfate scrubber. The scrubbing solution was a concentrated solution of vanadium(II) in 5–10% sulfuric acid solution over an ample supply of amalgamated mossy zinc. The vanadate solution was introduced into the bottle of the upward-flow reductor, passed through the reducing column at a rate of 25–50 ml per minute, and the reduced solution of vanadium(II) was received in the reservoir of the gravity-flow system. A siphon was created from the reservoir to the buret. The first buret-full of solution was discarded.

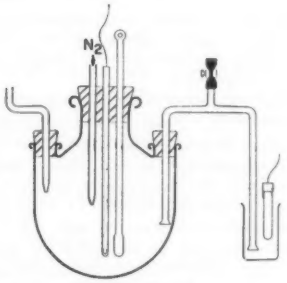

Figure 4. Titration flask.

A 25.00-ml aliquot of 0.1032 *N* potassium permanganate was pipetted into the titration flask and the liquid level was raised as needed by addition of oxygen-free water. Titration was carried out at 80°C using a Glas-Col heating mantle and a magnetic stirrer.

The titer of the vanadium(II) solution was checked over a period of several days. To assure homogeneity after standing, the solution in the reservoir was stirred by bubbling nitrogen through it. The solution in the siphon and buret was discarded. Results are given in Table I. The concentrations of vanadium(II) listed are for a three electron change, i.e., the first potential-break in titration of permanganate with vanadium(II).

Table I. Change in Concentration of Vanadium(II) with Time

Days:		0	2	3
Normality:		0.1736	0.1745	0.1730
Days:	4	5	7	12
Normality:	0.1721	0.1700	0.1703	0.1694

Proceedings of the

California Association of Chemistry Teachers

1961 Summer Conference

The California Association of Chemistry Teachers will hold its third summer conference on the teaching of chemistry at Asilomar, California, from August 20 to August 26, 1961. This third conference is open to all teachers of chemistry in the United States, as well as visiting teachers from foreign countries. Indications are that this conference will be even more successful than the first two.

An account of the first conference has appeared in these pages.[1] The 1960 conference, under the direction of Mr. James Ice, followed a similar pattern. Several of the "Recent Advances" series of papers have appeared in THIS JOURNAL.[2] Others are scheduled for publication. The CBA and CHEMS programs were the focus of much attention, as well as other innovations in high school chemistry teaching which are being accomplished on a more limited scale by members of the Association.

The third conference is being planned by Richard L. Miller of the Los Angeles City Schools. Complete details will be available about the end of June. Registration will begin at 4:00 P.M. Saturday, August 19, 1961; the conference will close on the afternoon of August 26, 1961.

The Recent Advances lectures will be on new topics by eminent authorities in their fields. Each lecturer will be present at the conference for at least two days and will be available for informal discussions. Participants will be divided into two groups for the morning and afternoon discussions; each group will consider two topics each day. Textbooks, laboratory manuals, atomic and molecular models, and other training aids will be available for examination. Facilities will be provided for interested groups who wish to view films and filmstrips during the late afternoon.

Tours and trips to points of scientific and historical interest will be planned. Swimming and other recreational facilities will be available. Accommodations include cottages and dormitories for single persons, married couples, groups, and families. Excellent meals are served in the large dining hall. Complete cost will be about $10.00 per day per person. The National Science Foundation is currently reviewing a request from the Association for financial support to include stipends for participants at the conference. In previous years these stipends have included travel, housing, and meals.

Point Lobos Reserve: "All this and chemistry too!"
Photograph: Courtesy of N. B. Drury

The conference staff is as follows:

Director	Mr. Richard Miller
Program Chairman	Dr. Jerome Holmes
Finance Chairman	Mrs. Joan Maxfield
Arrangements Chairman	Mrs. Dorothy Craig

For information, including applications for stipends, prospective participants should write to Mrs. Dorothy Craig, 1199 Laurel Street, Pasadena 2, California.

JOHN L. ABERNETHY
CACT Proceedings Editor

[1] THIS JOURNAL, **37**, 50 (1960).

[2] "New Aspects of Photosynthesis," by J. A. BASSHAM, THIS JOURNAL, **38**, 152 (1961) and "Gas Chromatography" by R. L. PECSOK, **38**, 212 (1961).

Asilomar Conference, August, 1960

Report of the New England Association of Chemistry Teachers

Joseph Weissbart
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Pittsburgh, Pennsylvania

Fuel Cells—Electrochemical Converters of Chemical to Electrical Energy

A fuel cell is a galvanic cell which converts the "free energy" of a fuel and oxidizing agent directly into electrical energy. We are familiar with two types of galvanic cells, primary and secondary, which store fuel and oxidizing agents in the cell itself. The electrical capacity of these cells depends on the quantity of chemicals stored. Primary cells, such as the Leclanche "dry cell," when discharged are discarded; secondary cells, such as the lead acid storage battery, when discharged can have the original store of chemicals regenerated by electrical charging. The fuel cell is similar in principle to these cells, with the important distinction that a fuel, generally a gas, and an oxidizing agent, generally oxygen, are continuously fed into and consumed in the cell.

Commercially available batteries, because of the chemicals they use as fuel and oxidizing agents, are expensive sources of electrical energy and are only useful where cheap conventionally generated electrical energy is not available or is not convenient for a particular requirement.

A heat engine is an essential feature in the conventional generation of electrical energy from fossil fuel. The efficiency of the conversion of heat to electrical energy by means of a reversible heat engine is limited by the second law of thermodynamics. The chemical energy stored in fossil fuels such as coal, and other carbonaceous fuels, is first degraded into thermal energy, only a portion of which can be converted to electrical energy. A modern central power station can attain a total efficiency of 42% of the available thermal energy of the fuel used. Most power stations operate at about 25% efficiency.

It also follows from the first and second laws of thermodynamics that any spontaneous chemical reaction (Gibbs free energy change $\Delta F < 0$) if made to discharge reversibly and isothermally in a galvanic cell can convert its available chemical energy into electrical energy with maximum efficiency.

From these thermodynamic considerations, Wilhelm Ostwald in 1894 proposed that the ideal way to produce electrical energy from coal would be to react coal and oxygen of the air in a galvanic cell (*1*). This hypothetical cell, operating very nearly reversibly and at ambient temperature, could convert the available heat of combustion of the carbon reaction to electrical energy with almost 100% efficiency.

Let us see, in principle, how such a reaction could take place in a fuel cell. The cell would consist of an oxygen-ion-conducting electrolyte, and two electrodes, the anode (negative electrode) at one electrolyte face and the cathode (positive electrode) at the other, in the form of a sandwich (Fig. 1). At the cathode-electrolyte interface the electrochemical reduction of O_2 takes place.

$$\text{Cathode reaction:}\quad O_2 + 4e^- \rightarrow 2O^= \qquad (1)$$

The oxygen ions migrate through the electrolyte to the anode electrolyte interface, where the reverse process, the electrochemical oxidation of oxygen ions, takes place.

$$\text{Anode reaction:}\quad 2O^= \rightarrow O_2 + 4e^- \qquad (2)$$

When the oxygen pressure at the cathode, ${}_cP_{O_2}$, is greater than the oxygen pressure at the anode, ${}_aP_{O_2}$, a spontaneous electrochemical transfer of oxygen from the high to the low pressure can occur.

$$\text{Net cell reaction:}\quad O_2({}_cP_{O_2}) \rightarrow O_2({}_aP_{O_2}) \qquad (3)$$

Under reversible and isothermal conditions of operation the maximum amount of electrical energy will be available at the load.

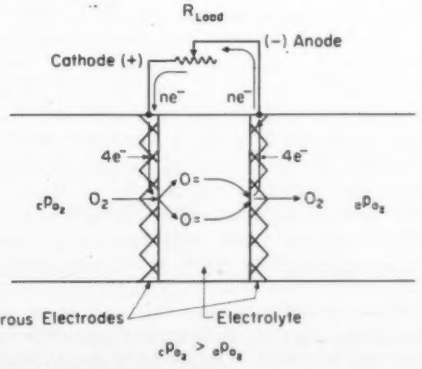

Figure 1. Oxygen concentration cell.

Presented at the 22nd NEACT Summer Conference, University of Maine, Orono, August, 1960.

The low oxygen pressure is maintained by reaction of oxygen with a fuel, in this case carbon, at or near the anode. The equilibrium conditions between carbon, carbon monoxide, and carbon dioxide, at the temperature of operation of the cell, determine the equilibrium pressure of oxygen. This type of cell is an oxygen concentration cell and can in principle use any fuel at the anode.

Unfortunately, conventional fuels such as coal and natural gas are chemically unreactive except at elevated temperatures. The use of these fuels in cells can only be considered at temperatures above 500°C., according to most investigators in this field. For operation near room temperature, hydrogen is the ideal fuel but is prohibitive in cost when compared with a cheap fuel such as natural gas.

One more important difference between batteries and fuel cells should be stressed. On current drain in batteries the electrolyte generally becomes diluted with reaction products, and the electrodes, which serve as electron conductors and fuel or oxidizing agent, are used up. In contrast, an ideal fuel cell transfers only $O^=$ ions (or, reduced oxygen in such ions as OH^- or $CO_3^=$) between chemically inert electrodes and without change of electrolyte composition.

Many different types of fuel cells are being investigated in laboratories throughout the world. They are generally classified as to temperature of operation, type of fuel burned, and whether reactions proceed directly in the cell or intermediate redox systems are used. We shall return to a discussion of this work.

History

The forerunner of all electrochemical devices can be considered to be the electric fishes which evolved in the ocean millions of years ago. A Mediterranean variety, the torpedo fish, capable of an output of up to 300 volts, was used in the first and second centuries B.C. by Greek and Roman physicians in the first recorded example of electric shock therapy. Ailments such as migrain headaches, epilepsy and gout were treated. The electric fishes passed out of fashion in the Middle Ages. They again became the vogue after the Renaissance and a large number of eminent biologists and physicists, among them Galvani, Volta, and Faraday investigated them.

Volta invented the first electrochemical battery, known as the voltaic pile, about the year 1800. It is noteworthy to mention that he described the voltaic pile or battery as an artificial torpedo because it resembled the column of plates of the torpedo electric organ with which he was familiar.[1] Nicholson and Carlisle in 1800 used the voltaic pile to decompose water electrolytically into O_2 and H_2. In 1839, Grove built the first fuel cell by supplying O_2 and H_2 to two platinum electrodes dipping in a sulfuric acid solution and obtained a deflection of a galvanometer (*2*). By using the voltage from several of these cells in series, he also decomposed water electrolytically (*3*).

Further work on H_2-O_2 cells has been pursued by many investigators. Studies on carbon-oxygen and other high temperature cells, during the years prior to the second world war, were mainly done by Emil Baur and co-workers (*4*). A review of H_2-O_2 and high temperature fuel cells is presented by Davtyan (*5*). A discussion of fuel cells and their possible applications, fuel sources, and estimated costs, is given by Young and Rozelle (*6*) and by Stein (*7*).

Thermodynamic Considerations

Consider a combustion reaction, e.g.,

$$CO + {}^1/_2O_2 \rightarrow CO_2 \qquad (4)$$

Let this reaction proceed by a net electrochemical process, i.e., by the formation of one mole of CO_2 in the cell and the transfer of two moles of electrons (2 $\mathfrak{F}$ coulombs of charge) from anode to cathode in the external circuit. During this process the temperature of the cell and the pressure and composition of reactants and product are held constant.[2] We now differentiate two heat effects: (I) q_1 the heat *absorbed* or *evolved*[3] in the cell and (II) q_2 equal to the i^2R_1t heat *evolved* in the load resistance R_1 for current i and time t for the formation of one mole of CO_2 (Fig. 2). The net heat *evolved* is the algebraic sum

$$q_{net} = q_1 + q_2 < 0 \qquad (5)$$

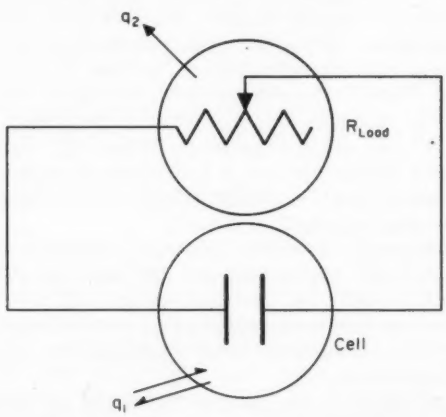

Figure 2. Distribution of heat q_3 (ΔH), between q_1, heat absorbed or evolved in the cell, and q_2 ($i^2R_{Load}t$) heat evolved at R_{Load}.

The value of q_{net} is a constant independent of the magnitude of the current (i.e., the rate of the cell reaction) and depends only on the formation of one mole of CO_2 under the conditions of operation of the cell as stated above. Therefore

$$q_{net} = \Delta H < 0 \qquad (6)$$

where ΔH is the enthalpy of the reaction (or heat of combustion) equal to the value obtained when the reaction, equation (4), is carried out directly.[4] The

[1] This material was taken from an excellent review concerning the influence of fashion on inventions in the field of electricity by Amberson, William R., *Amer. Scientist*, **46**, 33 (1958).

[2] Conditions of constant pressure and composition can be approximated in a cell with large electrode surfaces and large reservoirs of O_2, CO and CO_2, with, e.g., $P_{O_2} = 1$ atm at the cathode and $P_{CO}/P_{CO_2} = 1$ with $P_{CO} + P_{CO_2} \doteq 1$ atm at the anode.

[3] By convention, a negative sign is attached to the term if heat is evolved from the system, i.e., $q < 0$.

[4] For example, the value of ΔH of the direct reaction and the values q_1 and q_2 separately or the sum, q_3, of the electrochemical process, may be measured in a calorimeter.

distribution of q_{net} between q_1 and q_2 is a function of the magnitude of the current. The two limiting conditions are for short-circuit and reversible operation. At short-circuit, no electrical work is available, i.e., $q_2 = 0$ and all the heat, now the i^2R_et heat, where R_e is the internal cell resistance, appears as q_1. Therefore, from equations (5) and (6) and $q_2 = 0$,

$$q_1 = q_{net} = \Delta H < 0 \qquad (7)$$

At the other extreme, under reversible conditions of operation, i.e., at infinitely low current drain, the following values hold: q_1 is the reversible value, a maximum value for heat absorbed, $q_{1,rev} \geqslant 0$, or a minimum value for heat evolved $q_{1,rev} \leqslant 0$

$$q_{1,rev} = T\Delta S \qquad (8)$$

where T is the absolute temperature and ΔS is the entropy change for the reaction. Similarly, q_2 is $q_{2,rev} < 0$, a maximum value, equal to the i^2R_1t heat evolved (for very small values of i). Since $i^2R_1t = Eit$, the maximum electrical energy is obtained at the highest value of E, the cell emf, which is E_{rev}.

$$q_{2,rev} = \Delta F = -z\mathfrak{F}E_{rev} \qquad (9)$$

where ΔF is the Gibbs free energy change for the reaction, $z\mathfrak{F}$ is the total charge transferred at E_{rev}, $\mathfrak{F}$ is the faraday (96,500 coulombs) and z is the electrochemical valence change.

Equation (5) holds as well for the reversible values $q_{1,rev}$ and $q_{2,rev}$

$$q_{net} = q_{1,rev} + q_{2,rev} \qquad (10)$$

Substituting equations (6), (8) and (9), we obtain

$$\Delta H = T\Delta S + \Delta F \qquad (11)$$

which is the Gibbs-Helmholtz equation. ΔF or the algebraic difference between ΔH and $T\Delta S$ need only have a negative value for a galvanic cell reaction to be possible. In general, reactions of interest in fuel cells have $\Delta H \ll 0$, e.g., the heat of formation of H_2O is about 60 kcal.

For laboratory scale cells, the heat effects discussed above are rarely directly evident (but can be obtained indirectly from measurements of cell emf and their temperature coefficients.) For large-scale installations these effects are of critical importance in considering theoretical as well as practical fuel cell efficiencies. The thermodynamic efficiency, ϵ, is

$$\epsilon = \Delta F/\Delta H \qquad (12)$$

From the Gibbs-Helmholtz equation (*11*), three possibilities arise for ϵ:

(I) $\Delta S = 0$, $q_{1,rev} = 0$, then $\Delta F = \Delta H$ and $\dfrac{\Delta F}{\Delta H} = 1.0$.

(II) $\Delta S < 0$, $q_{1,rev} < 0$, i.e, heat is evolved in the cell, $\epsilon = \dfrac{\Delta F}{\Delta H} = \dfrac{\Delta H - T\Delta S}{\Delta H} < 1.0$. This heat if not ejected to the surroundings raises the temperature of the cell.

(III) $\Delta S > 0$, $q_{1,rev} > 0$, i.e., heat is absorbed by the cell from the surroundings, $\epsilon = \dfrac{\Delta F}{\Delta H} = \dfrac{\Delta H - T\Delta S}{\Delta H} > 1.0$.

In this instance if heat $-q_{1,rev}$[5] is not added from the surroundings, the cell cools down. The total thermal energy used $\Sigma q = q_{net} + (-q_{1,rev}) = q_{1,rev} + q_{2,rev} + (-q_{1,rev}) = q_{2,rev}$, which is equivalent to the maximum available electrical energy, equation (9). Therefore, theoretically calculated thermal efficiency can never be greater than 1.0 except in a hypothetical case, i.e., a cell reaction with $\epsilon > 1.0$ occurring at room temperature, where the surroundings can be considered as an infinite heat source. Table 1 shows values of E_{rev}, and ϵ at 298, 600 and 1000°K for several important fuel cell combustion reactions.

Table 1. Standard emf E and Efficiency $\epsilon = \Delta G/\Delta H$ of Combustion Reactions

Combustion reaction	z	—298°K— E	ϵ	—600°K— E	ϵ	—1000°K— E	ϵ
$C + O_2 = CO_2$	4	1.03	1.00	1.03	1.00	1.03	1.00
$2C + O_2 = 2CO$	4	0.74	1.24	0.86	1.48	1.02	1.78
$2CO + O_2 = 2CO_2$	4	1.34	0.91	1.18	0.81	1.01	0.69
$CH_4 + 2O_2 = CO_2 + 2H_2O$	8	1.04	1.00	1.04	1.00	1.04	1.00
$2H_2 + O_2 = 2H_2O$	4	1.18	0.94	1.11	0.88	1.00	0.78

We now return to a further discussion of the oxygen concentration cell (Fig. 1). We can visualize the oxygen transfer process as occurring in two separate steps: (I) the electrochemical step, i.e., the expansion of O_2 from a high partial pressure ($_cP_{O_2}$) to a lower partial pressure ($_aP_{O_2}$), equation (3). This is a spontaneous endothermic process for which the work of expansion is given by equation (11), with $\Delta H = 0$, i.e., ΔF (or $q_{2,rev}$) $= -T\Delta S$(or $-q_{1,rev}$), and

$$\Delta S = R \ln {}_cP_{O_2}/{}_aP_{O_2} > 0 \qquad (13)$$

(II) The oxygen at $_aP_{O_2}$ reacts directly with carbon in the anode chamber,

$$C + {}^1/_2O_2({}_aP_{O_2}) \rightarrow CO({}_aP_{CO} \cong 1 \text{ atm}) \qquad (14)$$

This is an exothermic process for which the heat of combustion of the reaction, $\Delta H = q_{net} < 0$, is available. The heat needed in step (I) is greater than the heat evolved in step (II), and therefore for the total process, the cell cools down. To operate the cell at constant temperature, further heat must be added from the surroundings. The thermal energy of CO reacting with O_2 could be utilized for this purpose.

The reaction of coal to form CO in a fuel cell presents more difficulties than that of burning gaseous fuel, i.e., CO or hydrocarbons. The following two-step chemical-electrochemical cyclical process appears to hold promise in utilizing the available energy in the carbon to CO_2 reaction:

Reaction outside of fuel cell: $CO_2 + C \rightarrow 2CO$, $\Delta H > 0$ (15)
(i.e., surroundings)

Reaction inside of fuel cell: $2CO + O_2 \rightarrow 2CO_2$, $q_1 < 0$ (16)
(i.e., system)

Net reaction: $C + O_2 = CO_2, \Delta H - q_1 = 0$ (17)
(i.e., system and surroundings)

The heat left over from the electrochemical reaction in the fuel cell, [equation (16), i.e., $q_{1,rev}$ *plus* i^2R_et heat *inside* the fuel cell for operation at $i \gg 0$] is to be used for the heat necessary for the endothermic reaction, equation (15) *outside* the cell. One CO_2, equation (16), is removed from the cycle before the CO is regenerated, equation (15). Theoretically the thermal efficiency can be 1.0. This type of system for

[5] $-q_{1,rev}$ (surroundings) $= +q_{1,rev}$ (system, i.e., cell).

upgrading or reforming CO as well as hydrocarbon fuels has been discussed by Gorin (*8*).

Kinetic Considerations

Gas Diffusion Electrode. All electrochemical reactions are heterogeneous, i.e., the electron exchange reaction occurs at the interface of two or more phases, e.g., metal/solution. For an electrode involving a gas as in fuel cells, e.g., Pt, O_2 the electron exchange reaction must occur at an electrode/electrolyte interface accessible to the gas. This type of an electrode is called a gas diffusion electrode. The three-phase reaction zone of such an electrode is necessarily only a line. Theoretically, the maximum number of such sites can be obtained by making the electrode in the form of a bundle of parallel capillaries of a uniform diameter. The liquid electrolyte enters at one end of the capillaries and the gas at the other. The three phase zone is where the meniscus makes contact with the metal and catalyst (Fig. 3). This can only occur for a certain capillary diameter, where the capillary pressure and the hydrostatic pressure is balanced by the pressure of the gas. When the gas forces the liquid

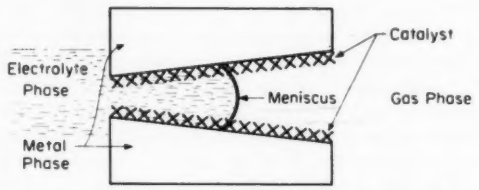

Figure 3. Idealized capillary structure of a gas-diffusion electrode.

entirely out of the capillaries or pores, "gassing" of the cell occurs. "Drowning" of the cell occurs if the gas is forced out of the capillaries or pores by the liquid. Practical gas diffusion electrodes are made from metal powder of two or more particle sizes sintered together (Fig. 4). Graded particle size or pore structure in graphite electrodes can be obtained by special techniques such as heat treatment in CO_2 atmosphere.

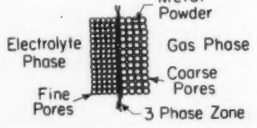

Figure 4. Metal powder double pore gas-diffusion electrode.

Polarization. When current is drawn from a cell the distribution of q_{net} between q_1 and q_2 is not any more than for the reversible case, equation (10). Some heat that should appear as part of q_2 in the form of electrical energy at R_1 is instead *evolved* in the cell and becomes part of q_1. This is the energy that is expended in overcoming the activation energy barriers associated with the various transport processes when the cell reaction is forced to proceed at a greater than negligible rate. Experimentally the loss of electrical energy for a certain current appears as a loss in voltage from the reversible value, i.e., $z\mathfrak{F}$ coulombs are transferred at $E < E_{rev}$. This loss in voltage is called polarization. Several types of polarization are distinguishable at least in principle. We shall discuss briefly concentration polarization, activation polarization and ohmic polarization. A typical current-voltage curve shows the net and the individual contributions (Fig. 5).

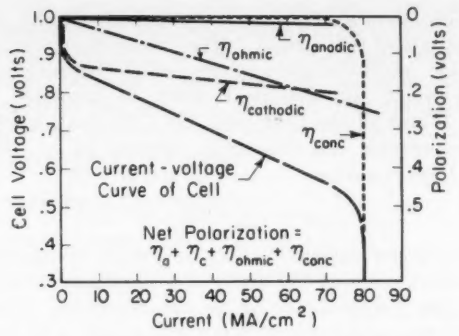

Figure 5. Operating characteristics of a hypothetical fuel cell.

When current is drawn from a cell, the reactant at the electrode is depleted and further reactant diffuses into the reaction zone from the bulk concentration zone. The loss in voltage or the concentration polarization is due to this difference in concentration at the interface. When the concentration at the interface drops to zero, i.e., all of the species diffusing to the interface react immediately, the cell voltage also drops to zero. This current is the diffusion limiting current (e.g., 80 ma. in Figure 5).

The loss in voltage on current drain due to the sluggishness of the exchange reaction at either electrode is known as (anodic or cathodic) activation polarization. When the rates in both directions (at the electrode) are equal to each other, equilibrium is established. This is accomplished by the formation of a charged double layer at the interface across which transfer of ions is hindered in one direction and aided in the other direction. The potential across this double layer is the reversible absolute electrode potential (not amenable to measurement except with respect to a defined reference electrode). The rate at equilibrium (in either direction) is known as the exchange current I_0. If I_0 is large and the activation energy for I_0 is low, a large current can be drawn with little loss of voltage. Electrode catalysts and increased temperature of operation reduce this polarization effect.

Ions must also be transferred across the electrolyte. An activation energy is associated with this process. The resultant voltage loss is the ohmic polarization or i^2R_c loss (R_c is the *internal* resistance of the cell). Mobility of the ions (if no electronic current is present) is proportional to the specific conductivity of the solution (conductivity per unit cube). The total conductivity also depends on the thickness and area of the electrolyte. Ohmic polarization is particularly serious with high temperature ceramic oxide electrolytes.

Fuel Cells Under Consideration

Hydrogen-Oxygen (KOH) Cells. These cells contain aqueous potassium hyroxide as the electrolyte. The electrodes are of the gas-diffusion type and are made from specially activated nickel or graphite to which catalysts are added. Cells may operate at slightly above room temperature at atmospheric pressure or may be pressurized and operate at 200–240°C (*9*, *10*). The electrochemical reaction does not proceed directly to water but to the hydrogen peroxide (HO_2^-) intermediate, which is further decomposed by catalysts to

Cathode Reaction:	(ideal) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	(18)
	(actual) $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	(19)
Anode Reaction:	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	(20)
Cell Reaction:	$O_2 + H_2 + OH^- \rightarrow HO_2^- + H_2O$	(21)
Decomposition Reaction:	$HO_2^- \xrightarrow{\text{catalysts}} {}^1/_2O_2 + OH^-$	(22)
Net Reaction:	${}^1/_2O_2 + H_2 \rightarrow H_2O$	(23)

oxygen and hydroxyl ions (*9*). The reactions are summarized above.

Hydrogen-Oxygen Ion Exchange Membrane Cells. These cells contain a solid organic membrane saturated with water as the electrolyte and operate at ambient temperature or slightly above (*11*). In cation exchange resin membranes, H^+ ions are mobile, while in anion exchange resin membranes, OH^- ions are the conducting species. Gas diffusion electrodes are made from platinum, nickel, and other metals. A schematic view of an an ion exchange membrane cell is shown in Figure 6.

Redox Cells. The redox cell principle involves the use of electrochemically active oxidant and reductant intermediates to utilize electrochemically sluggish fuel such as coal or hydrocarbons, and the oxygen of the air, at or near room temperature. The cell contains two liquid electrolytes (one for the cathode and one for the anode chamber) separated by a membrane permeable to a common ion such as H^+ or OH^-. Each electrolyte contains a dissolved reactant (reductant in the anode chamber and an oxidant in the cathode chamber). The products of the electrode reactions are circulated to the regenerator chambers (attached to each electrode chamber) where they are chemically reduced by the fuel and oxidized by the oxygen, respectively, and returned to the electrode chambers. Attempts in this direction have not been promising (*12, 13*).

Molten Salt (Carbonate) Cells. The electrolyte of this cell is a mixture of alkali carbonates contained in the capillary pores of a ceramic matrix. The cathode is made from silver powder and the anode is generally made from nickel powder to which catalysts are added. The construction of a laboratory test cell is shown in Figure 7 (*14*). The cell operates at temperatures at or above 500°C and utilizes CO and hydrocarbon fuels. Oxygen is transported as $CO_3^=$ ion (instead of $O^=$); therefore CO_2 must be present as a reactant at the cathode and is a product at the anode. The emf of the cell depends on the oxygen partial pressures as well as on the CO_2 partial pressures at the electrodes (*15*). The cell is an O_2 and CO_2 concentration cell similar in principle to the ideal oxygen concentration cell discussed above. The electrode equations and the relation between the emf of the cell and the pressures of O_2 and CO_2 at the electrodes are given below:

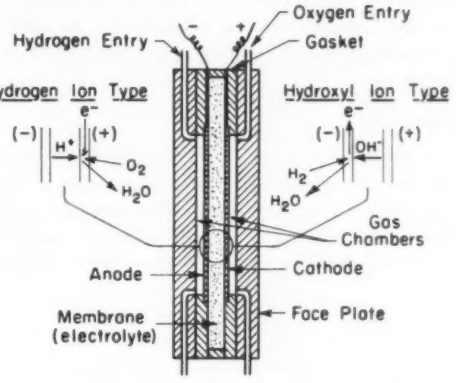

Figure 6. Hydrogen-oxygen ion exchange membrane fuel cell. [After Niedrach, reference (*11*).]

Solid Electrolyte (ceramic oxide) Fuel Cells. A high temperature fuel cell with an oxygen ion conductive electrolyte, based on the oxygen concentration cell principle (Fig. 1), is in the preliminary research stage at Westinghouse (*16*).

Hydrogen-oxygen fuel cells have the best operating characteristics of all fuel cells at present. The problem is to find ways to produce hydrogen more cheaply or to develop catalysts so that inexpensive carbonaceous fuels can be used.

High temperature fuel cells, although they can utilize low cost carbonaceous fuels, present serious development problems. During operation, changes in the electrode and catalyst structures occur and must be prevented. Direct reaction by leakage through the

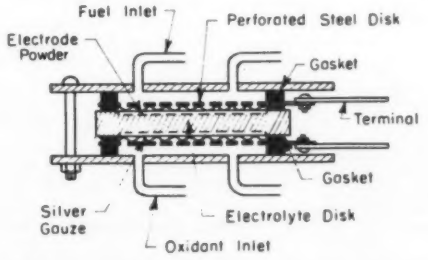

Figure 7. High temperature molten salt fuel cell. [After Broers, reference (*14*).]

Cathode reaction:	${}^1/_2O_2 + CO_2 + 2e^- \rightarrow CO_3^=$	(24)
Anode reaction:	$CO_3^= \rightarrow {}^1/_2O_2 + CO_2 + 2e^-$	(25)
Net cell reaction:	${}^1/_2O_2({}_cP_{O_2}) + CO({}_cP_{CO_2}) \rightarrow {}^1/_2O_2({}_aP_{O_2}) + CO_2({}_aP_{CO_2})$	(26)
	$E = \frac{RT}{4F} \ln \frac{{}_cP_{O_2}}{{}_aP_{O_2}} + \frac{RT}{2F} \ln \frac{{}_cP_{CO_2}}{{}_aP_{CO_2}}$	(27)

electrolyte or by electronic conduction (in ceramic oxides) is another problem. Side reactions and corrosion reactions occur readily. High power density and useful operating life are the two most important criteria for all fuel cells. The latter is especially difficult to obtain for high temperature fuel cells. The search for suitable construction materials to overcome these problems continues. Another problem for high temperature fuel cells is the construction of units of sufficient power density. As yet no high temperature fuel cell has been constructed that is even self-sustaining at the temperature of operation. An integrated fuel processing and fuel cell system also presents many problems.

Conclusion

Fuel cells have some unique features that offer many advantages for electrical power generation. They do not operate on a heat cycle and therefore are not limited in efficiency by this factor. Efficiency is independent of size over a wide range of power output, as contrasted with steam turbine generators which have lower efficiency at lower ratings. Fuel cells need not contain moving parts. Fuel cells are low voltage, high current devices of particular interest in the electrochemical industries such as the aluminum industry. Traction equipment could also be powered by low or moderate voltage direct current. Numerous special applications are possible where cost is of secondary importance.

An ideal fuel cell would use cheap fuels, be made of economical materials, operate at high efficiency, have high power density, and have long life. Low temperature fuel cells using hydrogen should begin to find special purpose applications within the next few years. The use of fuel cells for large power generation, i.e., central power stations, is still doubtful but is tantalizing enough at the present stage of development not to be entirely out of the question.

Acknowledgment

Helpful discussions concerning this manuscript were held with Dr. R. J. Ruka.

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Twenty-Third Summer Conference

August 21–25, 1961

University of Vermont, Burlington

Monday, August 21

7:30 p.m. "Chemistry on a Cosmic Scale," S. I. Gale.

Tuesday, August 22

9:00 a.m. "Do It Yourself—But Wear Goggles!" Paul Westmeyer.
"Only the Student Has No Gears," J. H. Day.

2:00 p.m. "Philosophy of Laboratory Instruction," N. D. Cheronis.
"Applications of Chromatography and Electrophoresis," P. R. Kasimer and H. J. Morowitz.

7:30 p.m. "Polaris, Sea Power, and National Defense," Commander T. R. Rhees, USN.

Wednesday, August 23

9:00 a.m. "Water and Aqueous Solutions," H. S. Frank.
"Applications of Chromatography and Electrophoresis," P. R. Kasimer and H. J. Morowitz.

Thursday, August 24

9:00 a.m. "The CHEM Study," J. A. Campbell.
"Meteorites and Cosmic Rays," Raymond Davis, Jr.

2:00 p.m. "The Examination of Trace Evidence, Chemical and Other Methods," J. L. Gormley.

7:30 p.m. "The Patent Office, the Patent System, and Chemistry," M. C. Rosa.

Friday, August 25

9:00 a.m. "Radical Chemistry," C. D. Cook.
"Gradient Elution and Ultra-Violet Absorption in Chromatographic Analysis," C. W. Gould.

2:00 p.m. "Inquisitive Chemistry—The Story of Chemical Analysis," D. I. Walter and O. R. Gates.
"Boranes and Rocket Fuels," C. J. Wiley.

Copies of the complete program and other information can be obtained from the Conference Secretary, Miss Constance L. Brown, University of Vermont, Burlington. Non-members are cordially invited to join the Association and attend the conference for a day or for the entire week.

Report of Committee on Status of the Teaching of Chemical Literature

The accompanying two tables summarize the statistical data collected by Professor M. G. Mellon, chairman of a joint committee of the Divisions of Chemical Literature and Chemical Education, appointed to study the status of the teaching of chemical literature. These data constitute the 55% response to 600 questionnaires sent to a representative sample of colleges training prospective graduate students and to all graduate schools of chemistry and chemical engineering.

Status of Instruction in Chemical Literature

Nature of instruction	Institutions granting Ph.D. Number	%	Institutions not granting Ph.D. Number	%
By means of formal course	42	53.2	92	36.6
Without a formal course	32	40.5	152	60.6
Considered unnecessary	5	6.3	7	2.8
	79	100.0	251	100.0

For the 134 institutions reporting, the following numbers show the credit hours of the various courses, and in parentheses, the corresponding number of institutions for each level of credit: 0 (2); ²/₃ (1); 1 (79); 1¹/₃ (5); 2 (39); 2¹/₃ (1); 3 (4); 3¹/₃ (1); 4¹/₂ (1); undesignated (1). The longer courses are partly technical writing, history of chemistry, and related topics.

Institutions Without Special Courses

Publications covered	32 institutions granting Ph.D. Number	%	152 institutions not granting Ph.D. Number	%
Periodicals	28	87.5	143	94.1
Patents	9	28.1	24	15.8
Government bulletins	0	0.0	7	4.6
Manufacturers' technical publications	6	18.7	39	25.7
Bibliographies	14	21.9	75	49.3
Indexes	25	78.1	115	75.7
Treatises	25	78.1	94	61.9
Monographs	26	81.2	86	56.6
Encyclopedias	20	62.5	83	54.6

The 184 institutions having no formal course depend upon a variety of means to introduce students to the literature. Some of those mentioned specifically (with the number of institutions so indicated in parentheses): Specific assignments (77); term papers (14); reports (3); assigned reading (6); "few" lectures, mostly in organic chemistry (12); course projects (13); directed study (3); course references (5); seminars (17); theses and research (28); laboratory preparations, projects, references, and reports (11).

Nominations for Office of Chairman-elect, 1961–62

EDWARD C. FULLER is Professor and Chairman of the Department at Beloit College. A graduate of Montana State with a Ph.D. from Columbia, he taught at Montana State, Bard (N. Y.), Champlain College (N. Y.), and the University of Wisconsin (summer school). He was President of Bard College, 1946–50. He has served the Division as Chairman of the Committee on the Teaching of Chemistry since 1955, and as a member of committees on films, visiting scientists, and the ACS-NSF *ad hoc* committee on the need for new approaches to high school chemistry. He was a participant at the Reed and Wesleyan conferences (which did the ground work for the CBA program) and at conferences on improving the college chemistry curriculum. Since 1956 he has served as Visiting Scientist to colleges and high schools. He is author of a dozen articles on chemical education, and has served on many NSF evaluation panels.

WENDELL H. SLABAUGH, Professor and Assistant Dean of Graduate School, Oregon State University, has served the Division as Program Committee and Institute and Conference Committee member, Visiting Scientist on the Division sponsored NSF program, and author of 13 papers and book reviews for the Journal of Chemical Education. He has directed and lectured in Summer Institutes and Academic Year programs and served on the state certification board for science teacher education. His Ph.D. at Washington State University followed industrial research in protective coatings. He has 21 research papers in colloids and surface chemistry, his major interest in teaching at the graduate level. He was selected outstanding campus teacher and was the lecturer in a 2-year experiment in general chemistry via television. He is active in ACS, AIC, Sigma XI, Phi Kappa Phi, and Phi Lambda Upsilon affairs.

Ballots will be mailed to members of the Division of Chemical Education and must be returned to the secretary by July 1, 1961. The present Chairman-elect, L. C. King (Northwestern), will become chairman after the fall ACS meeting. The present secretary, W. B. Cook (Montana State), serves until September 1962; the present Treasurer, W. G. Kessel (Indiana State Teachers), serves until September 1963. The member-at-large of the Executive Committee, R. H. Maybury (Redlands), serves until September 1962.

Chem Ed

BOOK REVIEWS

Chemical Periodicity

R. T. Sanderson, University of Iowa, Iowa City. Reinhold Publishing Corp., New York, 1960. x + 330 pp. Figs. and tables. 21.5 × 26.5 cm. $9.75.

If there were only one word permitted this reviewer to describe the book "Chemical Periodicity," it would have to be "useful." Professor Sanderson has incorporated a wealth of information in tables and charts in the text, much of which could otherwise be found only by consulting many different reference works and other sources in the chemical literature. The inclusion of a table of the many periodic charts at the beginning of the text is most useful. The inclusion of a table of "Tables" would also be helpful, and it is hoped that such will appear in future editions.

If the reviewer were allowed a second word of description, it would be "unusual." The author's approach is unusual, from the table of contents (a cross-sectioned Condensed Partial Index) onward, and much of this originality is pedagogically effective, e.g., the use of several periodic charts with circles of appropriate size to represent relative radii and atomic volumes of atoms. Although this reviewer disagrees with the use of this device to represent certain physical properties, such as heats of formation and densities, because the relatively small circles representing the alkali metals in such cases can lead to confusion for some students who might infer that these atoms are relatively smaller in size than atoms following them horizontally, when actually the reverse is the case.

Excellent photographs of molecular and crystal models have been included in the text, but this reviewer hopes that in future editions it will be possible to label the different atoms in some way, because the black and white photography might sometimes make it difficult for students to tell which atoms are which.

The value of the book is enhanced by the inclusion of both a subject and author index, although these have been combined into a single index. Errors (e.g., the electronic structure of gadolinium on page 12) are bound to creep into texts where considerable detail is involved, and it is to be hoped that these will be eliminated in future editions. This reviewer recommends this book to teachers of a junior or senior course in inorganic chemistry, either as a text or important source reference. The originality of approach is certain to be of interest.

The page size of the book is fairly large (almost $10^1/_2$ inches high) but the many tables and charts may have something to do with this, and in the main, their value far outweighs the inconvenient page size.

STANLEY KIRSCHNER
Wayne State University
Detroit, Michigan

Reviewed in This Issue

R. T. Sanderson, Chemical Periodicity
Francisco Bermejo Martinez and *Antonio Prieto Bouza*, Aplicaciones Analíticas del AEDT y similares
F. Din and *A. H. Cockett*, Low-Temperature Techniques
Martha E. Munzer and *Paul F. Brandwein*, Teaching Science Through Conservation
A. A. Lumsdaine and *Robert Glaser*, Editors, Teaching Machines and Programmed Learning
William Cahn, Einstein: A Pictorial Biography
Alfred Burger, Editor, Medicinal Chemistry
Albert Szent-Györgyi, Introduction to a Submolecular Biology
Joseph H. Simons, A Structure of Science
M. J. Buerger, Crystal-Structure Analysis
Arthur W. Adamson, Physical Chemistry of Surfaces
Robert S. Harris and *Harry von Loesecke*, Editors, Nutritional Evaluation of Food Processing
Raymond E. Kirk and *Donald F. Othmer*, Encyclopedia of Chemical Technology. Second Supplement Volume
K. A. Brownlee, Statistical Theory and Methodology in Science and Engineering
E. H. B. Pietsch, Editor, Gmelins Handbuch der Anorganischen Chemie. 8 Auflage. System Nummer 33, Cadmium, erganzungsband
J. R. Partington, A Short History of Chemistry

Aplicaciones Analíticas del AEDT y similares

Francisco Bermejo Martinez, Universidad de Santiago de Compostela, and *Antonio Prieto Bouza*, Químico de La Toja, S.A. Imprenta del Seminario Conciliar, Santiago de Compostela, Spain, 1960. xii + 629 pp. Figs. and tables. 17 × 24 cm. $10.

Ethylenediaminetetraacetic acid (EDTA) and related compounds, now often termed *chelons*, are developing a specialized literature more rapidly and more extensively than any previous organic analytical reagent. Hence, both the specialist and the applied analyst welcome each new monograph on chelons. The work by Drs. Bermejo and Prieto carries the literature into 1959 and strikes a fine balance between consideration of relevant theory and basic information and the presentation of ready-to-use facts and procedures. The authors are active researchers. The work often reflects their personal studies and includes findings unpublished by them at the time the manuscript was completed.

The authors in the early chapters consider the properties of the chelons, their use in titrimetry and colorimetry, and their application, usually as masking agents, in diverse separations and determinations. The last chapter, consisting of 254 pages, presents procedures employing chelons in the determination of various anions, cations, and some organic compounds, both in simple systems and complex matrixes, especially alloys. Critical notes appended to many procedures attest to the authors' personal experience.

The bibliography cites 1278 references; the reviewers, based on their own bibliographic efforts, can state that a satisfying degree of completeness has been achieved. An adequate subject index is provided and through its use even brief statements in the text may be often located.

U. S. technologists often neglect significant works in languages in which they have only limited proficiency, and thereby sidestep the opportunity to gain proficiency! The monograph by Bermejo and Prieto is in Spanish, a language of which the reviewers have only limited command. A microappreciation of Spanish grammar, a semimicro vocabulary (500–600 basic words and the relevant chemical jargon, for example, *valoración* = titration), and occasional resort to a pocket dictionary will suffice for the experienced chemist to follow the directions presented, especially because of the numerous English cognates. This is the experience of the reviewers in almost daily reference to the work over a period of some weeks.

This monograph is commended to researchers studying chelons and organic analytical reagents generally and to chemical analysts as a valuable point of entry into the literature of a salient area of advance in contemporary analytical chemistry.

A. J. BARNARD, JR.
and W. C. BROAD
J. T. Baker Chemical Co.
Phillipsburg, New Jersey

Low-Temperature Techniques

F. Din and *A. H. Cockett*, both of British Oxygen Research and Development, Ltd. Interscience Publishers, Inc., New York, 1960. viii + 216 pp. Figs. and tables. 14.5 × 22.5 cm. $6.50.

This book covers such topics as producing and measuring low temperatures, low temperature techniques in the laboratory, properties of materials at low temperatures, gas separation, and storage, transport, and use of liquefied gases. Drawings of apparatus which are used to illustrate the subject matter are mostly schematic and are, in general, well done.

In following a historical approach to the subject matter, the authors devote too much space to the situation existing prior to World War II and not enough space to the developments after World War II associated with the appearance of the Collins helium cryostat and the demands for relatively large quantities of liquid hydrogen and other liquefied gases.

Mathematical as well as other descriptive detail has been kept to a minimum. As a result, the authors have produced a simply written text which should serve as an introduction to the low temperature field. However, for workers contemplating or doing research at low temperatures, the insufficiency of detail is a handicap. For these research workers, there are a number of recent books on low temperature techniques such as R. B. Scott's "Cryogenic Engineering" or G. K. White's "Experimental Techniques in Low Temperature Physics" which are more useful.

E. L. Pace
Western Reserve University
Cleveland, Ohio

Teaching Science Through Conservation

Martha E. Munzer and *Paul F. Brandwein*, both of the Conservation Foundation. McGraw-Hill Book Co., Inc., New York, 1960. xvii + 470 pp. Figs. and tables. 16 × 23.5 cm. $7.50.

This is a book for teachers of science—one of a series devoted to curriculum and methods in education published by McGraw-Hill. The authors accept as the likely pattern for the future the present practice of the schools of teaching about the problems of use and management of natural resources in several different subjects, including science. From this point of view, conservation, which in this book is synonymous with utilization and management of natural resources, is a prevading theme running through much of the total school program. The title of the book reflects this point of view.

Well over 95 per cent of the 447 pages are devoted to procedures and activities for teaching science. The topics on which several hundred specific teaching suggestions are offered range the entire field of secondary school science. The book has several features designed to make it an effective tool for the teacher. For example, there are two tables of contents. One is keyed to important facets of conservation; the other, to the separate science subjects. There are numerous cross references. The index is well done. An entire chapter is devoted to specific information on materials required for experiments, sources of equipment and supplies, and films. There is a good bibliography of reference sources.

As one turns the pages, he may be startled to find that on many, there are no references to conservation. To this reviewer, however, this appears good in the sense that a sound appraisal of problems of conservation must be based on a clear understanding of processes and interrelationships existing in the natural environment. The authors have attempted to make a bridge between scientific understandings and concepts of conservation by numerous statements highlighted in bold print.

The natural resources needed to support a dynamic, and technologically-based society are by no means fixed, nor are the problems of their use and management static. The authors are to be commended for making this principle a theme of their book and for recognizing the relationship of science and technology both to the development of, and the solution of conservation problems. A chapter is devoted to science education for the potential scientists and technologists, whose intellectual capabilities represent a resource upon which the solution of conservation problems depends.

This book is recommended to teachers of secondary school science as a valuable soure eof specific ideas on teaching science. It also is a good book on the methodology of teaching science. It does show well how science can contribute to desirable attitudes toward, and understandings of conservation. Probably, it will not convert the teacher who is not conservation minded into one who is, but that is not stated as a purpose.

Ralph E. Keirstead
State Department of Education
Hartford, Connecticut

Teaching Machines and Programmed Learning

Edited by *A. A. Lumsdaine*, University of Southern California, Los Angeles, and *Robert Glaser*, University of Pittsburgh, Pennsylvania. Department of Audio-Visual Instruction, National Education Association, Washington, D. C., 1960. xii + 724 pp. Figs. and tables. 15× 23 cm. $7.50.

Teaching machines offer a valid new approach to tutorial instruction adapted to the needs of the individual student. With a properly designed teaching machine program the student proceeds at his own pace, is always active in his participation, learns the results of his work as he progresses—and if the program is a good one—the student *knows* all the material when he has finished.

This book is the first complete book on the subject and is indeed the best possible introduction to the subject. It consists of 47 articles written by most of the important names in the field. Not only is there a complete historical introduction, but the important original papers are reprinted. The discussion of the different kinds of programs is complete and thorough as is the discussion of learning theory and reports on completed experiments. Of great value are the sober second thoughts and criticisms; problems to be solved and possible pitfalls are well aired. The various types of machines commercially available are described as well as the ones which may easily be constructed by the teacher.

One hundred nine pages of Appendix I are devoted to abstracts of all the articles on the subject printed to date (and even some which have been presented but not published). The abstracts are unusually complete and readable. Appendix II is a 28 page bibliography.

The book is the best place to start for the reader interested in learning about teaching machines. It is indispensable for any one in the field and will certainly be the major source book for many years to come.

This book is recommended enthusiastically and without reservation.

Jesse H. Day
Ohio University
Athens

Einstein: A Pictorial Biography

William Cahn. The Citadel Press, New York, 1955; first paperback reprint, June 1960. 128 pp. Illustrations. 18 × 25 cm. $1.25.

This is a book of beautiful and interesting pictures about Einstein. Unfortunately, comments accompany these pictures. And while Einstein's photogenic face and his inspiring life are sufficient to redeem almost any text describing them, there seems to be no excuse for the gross errors which mar this one, especially in a reprint edition appearing five years after the original.

Some of these errors represent only misleading incompleteness, as in the figure on page 75 which is described as showing Einstein, a daughter, son-in-law, wife and "friends," while these "friends" include another daughter and her husband. A much grosser error appears on pages 44–45 where a picture purporting to show Einstein's first American press conference in 1921 was actually taken during his later trip in 1930–31. I confirmed this point with the lady shown in the picture who had not set foot in the U.S.A. before that date.

Especially shocking is the reproduction on page 27 of the first page of "the original printing of Einstein's famous theory of relativity" which, in fact, is his work on Brownian motion which appeared on page 549 of the same volume in which the theory of relativity is printed on page 891.

Certainly one can expect an author to have enough familiarity with his subject or to get competent enough advice to avoid such blunders and it should be the duty of a responsible publisher to see to it that he does.

Karol J. Mysels
University of Southern California
Los Angeles

Medicinal Chemistry

Edited by *Alfred Burger*, University of Virginia, Charlottesville. 2nd edition. Interscience Publishers, Inc., New York, 1960. xiii + 1243 pp. Figs. and tables. 19 × 26 cm. Trade edition, $37.50, college edition, $27.50.

Medicinal chemistry is concerned with naturally-occurring and synthetic compounds which may be used in medicine for the treatment of disease. This includes isolation, characterization, and determination of the structure of natural products, as well as the synthesis of clinically useful drugs. Medicinal chemists are also concerned with the biological mechanisms which explain the activity of drugs, and with attempts to relate molecular structure to physiological activity. The science had its beginnings with the work of Paul Ehrlich, at the end of the nineteenth century, but progress was relatively slow until World War II. Since then tremendous strides have been made. These may be reflected in the enormous gain in life expectancy since 1940. Most of the progress in this field was described in specific monographs, until in 1951 the definitive survey of this field, by Alfred Burger, was published in two volumes.

The present volume is the second edition of this earlier work. During the interval since the appearance of the first edition, so much has happened in the field that it would have been extremely difficult for one man to review it accurately. Burger is to be commended for his willingness to share the honors of authorship, already his by right of the success of the first edition, with 34 coauthors in the second edition, thus getting expert help in reviewing specialized areas. The second edition has been enlarged from 43 to 55 chapters, to include many new areas not even considered as medicinal chemistry 10 years ago, such as Psychopharmacologicals (Chapter 18) and Drugs for Irradiation Sickness (Chapter 55).

The second edition retains the organization of the first. The first nine chapters present a historical introduction and a broad theoretical background. Such subjects as "Response of Cells and Tissues to Drugs," by D. R. H. Gourley (Chapter 5), "Relation of Chemical Structure and Biological Activity," by Burger (Chapter 6), and "Metabolite Antagonism," by C. Kaiser (Chapter 9) serve to introduce the reader to the later special topics. These later chapters deal with special classes of drugs, which are arranged according to their medicinal uses. The pharmacodynamic agents are discussed in Chapters 10 through 39. Chapter 10, by A. F. Wagner and Karl Folkers, deals with the Vitamins. Chapter 37, by S. B. Barker, Chapter 38, by William R. Nes, and Chapter 39, by G. W. Anderson, deal with the Thyroid, Steroid, and Protein Hormones, respectively. The chapters between cover the many synthetic drugs and natural products acting on the various functions of the body. Chapter 40 offers an "Introduction to Chemotherapy," by Alfred Burger. The following 13 chapters discuss the various agents used against invading organisms, including the "Chemotherapy of Neoplastic Diseases" (Chapter 50) by Dean F. Gamble, Howard Bond, and Alfred Burger, and "Antiviral Drugs" (Chapter 51) by R. G. Child. Chapter 54 concerns "Tracers in Pharmaceutical and Medicinal Studies," by Maxwell Gordon.

This volume represents the most comprehensive coverage of the field of Medicinal Chemistry available in one cover. The text is clear and readable and many useful tables improve its use as a reference. The emphasis is on the organic chemistry of drugs, and the text is profusely illustrated by structural formulas, which are remarkably free from error, considering the enormous number involved. Although the book is addressed to the more advanced reader, it provides a useful reference for any chemist. It is especially useful in tracing any specific drug, and determining its structure or chemical name from its proprietary or generic name.

E. Campaigne
Indiana University
Bloomington

Introduction to a Submolecular Biology

Albert Szent-Györgyi, Institute for Muscle Research at the Marine Biological Laboratory, Woods Hole, Massachusetts. Academic Press, Inc., New York, 1960. x + 135 pp. Figs. and tables. 14.5 × 22.5 cm. $5.

This book of 135 pages is recommended for those who wish to share the insights of a mind which is recognized as one of the most penetrating of our generation.

The chapter headings include Why Submolecular Biology?, The Energy Cycle of Life, Units and Measures, Electronic Mobility, Problems of Charge Transfer, On the Mechanism of Drug Action, on ATP, and On the Chemistry of the Thymus Gland. In the concluding chapter on The Living State the author presents many of his seasoned perspectives. The entire book focusses on the electronic level of biochemistry.

Among Szent-Györgyi's many talents is the ability to compress a large area of thought into one or a few colorful sentences which pentrates to the heart of the matter. A few of these follow. "Physics is the science of probabilities." "Biology is the science of the improbable." "One of the basic principles of life is "organization" by which we mean that if two things are put together something new is born, the qualities of which are not additive and can not be expressed in terms of the qualities of the constituents." "What admits no doubt in my mind is that the Creator must have known a great deal of wave mechanics and solid state physics, and must have applied them. Certainly, he did not limit himself to the molecular level when shaping life just to make it simpler for the biochemist." "Research is rarely guided by logic. It is guided mostly by hunches, guesses, and intuition. All the same, once we get somewhere and present our results, we like to present them as a logical sequence."

Appropriately, the closing lines are, "We will really approach the understanding of life when all structures and functions, all levels, from the electronic to the supramolecular, will merge into one single unit. Until then our distinguishing between structure and function, classic chemical reactions and quantum mechanics, or the sub- and supramolecular, only shows the limited nature of our approach and understanding."

Sidney W. Fox
The Florida State University
Tallahassee

A Structure of Science

Joseph H. Simons. Philosophical Library, Inc., New York, 1960. x + 269 pp. 15 × 22 cm. $4.75.

In the preface, the author indicates he is a very modest person. He declares that the whole book is an experiment. There is no list of references, because "the author feels incompetent to provide an adequate one," and he "may misquote or at least misinterpret the valued subject matter." There is no index.

The book is divided into three parts. Part 1 attempts to explain the nature of science and scientists, and the interaction of science with other areas of human knowledge and experience. The author's philosophy emerges as a belief that although science is amoral, the philosophy that stems from it is essentially ethical; although science can only strive for the truth, science provides a way of life which is true and beautiful; although science has created problems in human relationships, the only way out is the utilization of more science.

Part 2 is essentially an elementary qualitative description of some of the concepts of science, such as force, energy, inertia, plus some discussion of time and space considered as abstractions.

Part 3 opens with examples which the author cites as evidence that the philosophical interpretation of scientific theory contains many elements of disorder and and confusion. This section embodies the primary purpose of the book, by presenting a number of speculations which the author hopes may lead to resolving some of the inconsistencies. He is very candid with his readers, warning them that his speculations are not to be dignified as scientific theories, or even hypotheses, but are to be considered as "only dreamed up relationships or postulations that have either stimulated thought or provided a feeling of greater satisfaction with the laws of science."

The lack of confidence engendered by the author in his preface and the declared lack of originality combine to make this book unattractive reading. The style is boresomely repetitious, frequently disorganized, and spotted with irrelevancies. In fact, much of Part I is not connected with the primary objective of the book as presented in Part III.

Mel Gorman
University of San Francisco
San Francisco, California

(*Continued on page A364*)

BOOKS FROM INTERSCIENCE

An Introduction to the Chemistry of Heterocyclic Compounds

by **R. M. ACHESON,** *Oxford*

This text for the graduate or senior undergraduate level will be welcomed by teaching organic chemists who, in the past, have often had to rely upon special lectures to introduce this complex subject. It is a concise account of the more important properties and chemical reactions of basic heterocyclic systems, using modern electronic systems and mechanistic concepts where possible. Recent biochemical developments are brought into the presentation when appropriate. The author's wide experimental and teaching experience is combined in an astute selection of material and a treatment which brings the flavor of the research laboratory into the classroom.

1960 356 pages $5.00

Name Index of Organic Reactions

by **J. E. GOWAN,** *Lecturer in Organic Chemistry, University College, Dublin* and **T. S. WHEELER,** *Professor of Chemistry, University College*

A complete rewriting and expansion of the much smaller 1950 edition, originally prepared by the Society of Chemical Industry. This new compilation contains nearly 750 named reactions. Formulas have been added and the literature citation has been increased to include papers which have appeared in the last ten years. Articles in standard reference works have been noted, and a supplementary index has been added which provides readily available information on methods for the synthesis of compounds containing various functional groups. A useful and time-saving tool for both the student and practicing chemist, and for anyone involved with the literature of organic chemistry, who may, for instance, wish to investigate the nature of the Ostromyslenskii reaction.

1960 256 pages $8.50 (U. S. A. only)

Physics and Archeology

by **M. J. AITKEN,** *Research Laboratory for Archeology and the History of Art, University of Oxford*

This book describes some of the ways in which physics has been applied to archeology. It is intended both for the general scientific reader and for the student of archeometry—measurements made on archeological material—and it emphasizes methods which produce objective, quantitative results. The chapters have been carefully sectionalized, so that a reader may omit a part he finds too technical without fear of losing his track, and copious references to original papers have been included for those wishing to pursue things further. The main subjects discussed are: Finding—Magnetic Location—The Proton Magnetometer—Resistivity Surveying—Dating—Radiocarbon Dating—Magnetic Dating—Analysis.

1961 194 pages $6.00

Basic Principles of Fission Reactors

by **W. R. HARPER**

This book will take the reader to about the stage at which detailed reactor design begins, without assuming any previous knowledge of nuclear technology. However, an appropriate background of physics, mathematics, and some chemistry, is required. The first two chapters introduce important ideas in nuclear engineering new to the reader, which permits description of a nuclear power station early in the book. The reactor itself is the centerpiece. Attendant subjects such as radiation protection, health physics, waste disposal, and economic implications are discussed in enough detail to put the reactor in perspective. Though designed as an introduction to a postgraduate course, *Basic Principles of Fission Reactors* is appropriate for the undergraduate well-prepared to proceed to a higher degree in science or technology, and it also provides a coherent account of reactors to those professionally qualified in neighboring fields.

1961 324 pages $7.50

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An Introduction to Basic Unit Operations

A. A. BENEDETTI-PICHLER, *Queens College, New York*

A highly useful textbook, laboratory manual, and reference work for organic and inorganic analysis. Book provides a comprehensive treatment of quantitative analysis with special emphasis on accuracy in manipulative techniques and understanding of unit operations. Adaptable to all levels of instruction, book includes numerous illustrations and reference tables. *"Impressive...thorough, and firmly based on valuable practical detail."*—**The Chemical Age.** *"A wonderful text and reference book."* —H. D. RHODES, *University of Arizona. 1956. 666 pp.* $12.50

The EVOLUTION of CHEMISTRY

EDUARD FARBER

This absorbing study of the origin and history of chemistry provides a fuller understanding of its concepts and methods by integrating its evolution with progress made in other sciences and philosophies. Book shows how the development of theories and the use of experiments have led to our present knowledge of the true nature of atoms, molecular structure, affinity, and chemical reactions. *"Chemists have reason to be grateful to Dr. Farber for having written a well-balanced, scholarly work."*—**Journal of the Franklin Institute.** *1952. 349 pp.* $6

ISOTOPE EFFECTS on REACTION RATES

LARS MELANDER, *Nobel Institute of Chemistry, Stockholm*

New. This authoritative volume serves as an introduction to and theoretical survey of the field of kinetic isotope effects, with emphasis on principles. Based on the theory of absolute reaction rates, current formulas for the prediction of kinetic isotope effects from molecular data are developed. The problems encountered in the evaluation of isotope effects from experimental data are discussed; the most important relationships are diagrammed. Simple reactions are used to illustrate the general degree of agreement that may be expected between empirical and predicted isotope effects. *1960. 181 pp.* $6.00

A volume in a series of monographs, *Modern Concepts in Chemistry*, prepared under the editorship of Bryce Crawford, Jr., Dean of the Graduate School and Professor of Chemistry, University of Minnesota; W. D. McElroy, Chairman, Dept. of Biology and Director, McCollum-Price Institute, Johns Hopkins University; and Charles C. Price, Director, John Harrison Laboratory of Chemistry, University of Pennsylvania.

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BOOK REVIEWS

Crystal-Structure Analysis

M. J. Buerger, Massachusetts Institute of Technology, Cambridge. John Wiley & Sons, Inc., New York, 1960. xvii + 668 pp. Figs. and tables. 16 × 23.5 cm. $18.50.

In this book Buerger has achieved a high degree of detail by careful restriction of subject matter. He assumes that the reader understands the process of obtaining X-ray diffraction data and the method of determining the unit cell and space group, as described in his "X-ray Crystallography." The present book describes the measurement of intensities and the methods of deriving from these data the positions of the atoms in the unit cell. The more advanced methods of interpretation of the Patterson function are not discussed in detail because they are the subject of a companion book by the same author, "Vector Space and Its Application in Crystal-Structure Investigation." The theory behind these procedures is presented, as are practical procedures to be followed.

There is an excellent discussion of the physical requirements of crystals suitable for study. For example, danger signals for the existence of twinning are described. The physics of diffraction is treated extensively, especially with respect to its geometrical properties. Very detailed descriptions are given of several simple structure determinations. Certain difficulties which occur in more complicated cases are illustrated by specific examples. In the development of Fourier theory, the concept of the inverse structure is carefully presented. The discussion of the phase problem is a clear and concise introduction to what is perhaps the most controversial aspect of crystallography.

In all of these subjects the theory is derived from a sufficiently elementary start and by simple enough steps so that an average graduate student in physical science should be able to follow the discussion without difficulty. The author mostly avoids the use of the symbols of vector algebra. On the other hand, familiarity with the conventions for representation of symmetry is assumed throughout. In some cases the discussion reaches rather advanced topics. Each chapter is followed by an extensive list of references for further details.

Though considerable space is devoted to older methods of making Fourier calculations, Buerger gives scant attention to the modern digital computers which are becoming dominant in crystallographic computations. The discussion of intensity correction factors for direct-counting methods is rather superficial. With these exceptions, the choice of topics is excellent.

Physically the book is very attractive with many clear diagrams and illustrations.

The general level and subject matter make this book suitable for careful study by one who is beginning work in crystal-structure analysis. There are many

(*Continued on page A366*)

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INTRODUCTION TO CHEMICAL ENGINEERING

By L. BRYCE ANDERSON, The Rice Institute; and L. A. WENZEL, Lehigh University. The McGraw-Hill Chemical Engineering Series. Ready in June, 1961.

Designed for a fast-paced, rigorous one semester course to introduce the sophomore to the chemical engineering profession and to the chemical process industries. The authors' objective is to cover the topics usually covered in stoichiometry, but also to give the student knowledge of and enthusiasm for the field of chemical engineering, so he will have a greater sense of purpose as he proceeds through subsequent courses.

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By F. J. C. ROSSOTTI and HAZEL S. ROSSOTTI, University of Edinburgh. McGraw-Hill Series in Advanced Chemistry. Ready in August, 1961.

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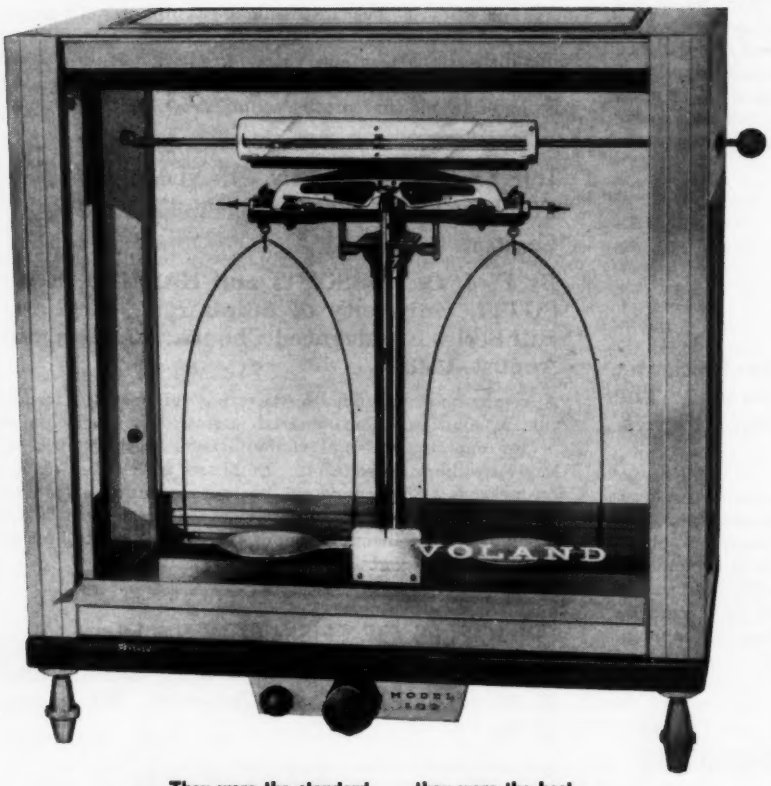

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BOOK REVIEWS

sections which could be studied with profit by rather experienced crystallographers. While it is perhaps too specialized to be suitable as the textbook of a first course in crystallography for students not planning research in that field, much of it would be excellent collateral reading for such a course.

DAVID H. TEMPLETON
University of California
Berkeley

Physical Chemistry of Surfaces

Arthur W. Adamson, University of Southern California, Los Angeles. Interscience Publishers, Inc., New York, 1960. xiv + 629 pp. Figs. and tables. 16 × 23.5 cm. $12.75.

For students of all kinds this book would provide a good reference to the more "classical" parts of the subject. The approach is that laid down by the late Professor W. D. Harkins of Chicago some 20 years ago. Perhaps the selection of topics might be defended as the result of a sharp distinction between physical chemistry and chemical physics, but in any case the result has been to exclude most of the topics of intense current research activity: microscopy of thin films, kinetics of crystal growth, semiconductor surfaces, surface states and catalysis, grain boundaries in solids, etc.

Slightly less than one-third of the book is devoted to capillarity, liquid-gas interfaces, and surface films on liquids. The treatment would serve as excellent background material for the usual experiments on the subject in the elementary physical chemistry laboratory. The electrochemical aspects of surfaces are summarized in a 50-page chapter, but irreversible thermodynamics is not introduced. Chapter V discusses the surfaces of solids in 80 pages without much logical organization. It starts with a vague account of sintering. There follow, however, adequate discussions of the surface tension of solids and contact angles. The subject of chemical reactions of solid surfaces is allotted only four pages. A short section on nucleation and crystal growth is old fashioned, and seems to miss completely the important point that spontaneous nucleation is practically impossible. There are short, interesting chapters, with a technical slant, on friction and lubrication, wetting and detergency, emulsions and foams. The adsorption of gases on solids and its use in estimating surface areas are treated extensively in 100 pages. This discussion is detailed and accurate, but there are serious omissions, such as gas chromatography and the many valuable applications of statistical mechanics. The book concludes with short chapters on catalysis and adsorption from solution.

All in all, this book is rather uneven. There is no doubt that it will be a useful reference for the material on capillarity and surface areas. The rest of the book

(*Continued on page A368*)

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By WILLIAM F. LUDER, Ph.D., Professor of Chemistry; ARTHUR A. VERNON, Ph.D., Professor of Chemistry; and SAVERIO ZUFFANTI, Professor of Chemistry, Department of Chemistry, Northeastern University, Boston, Mass. 582 pages, 6" x 9¼", with 149 illustrations. $6.75. *Second Edition*

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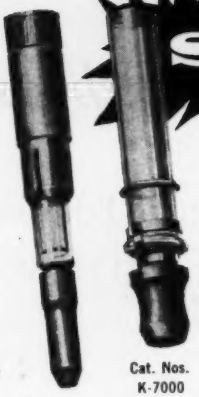

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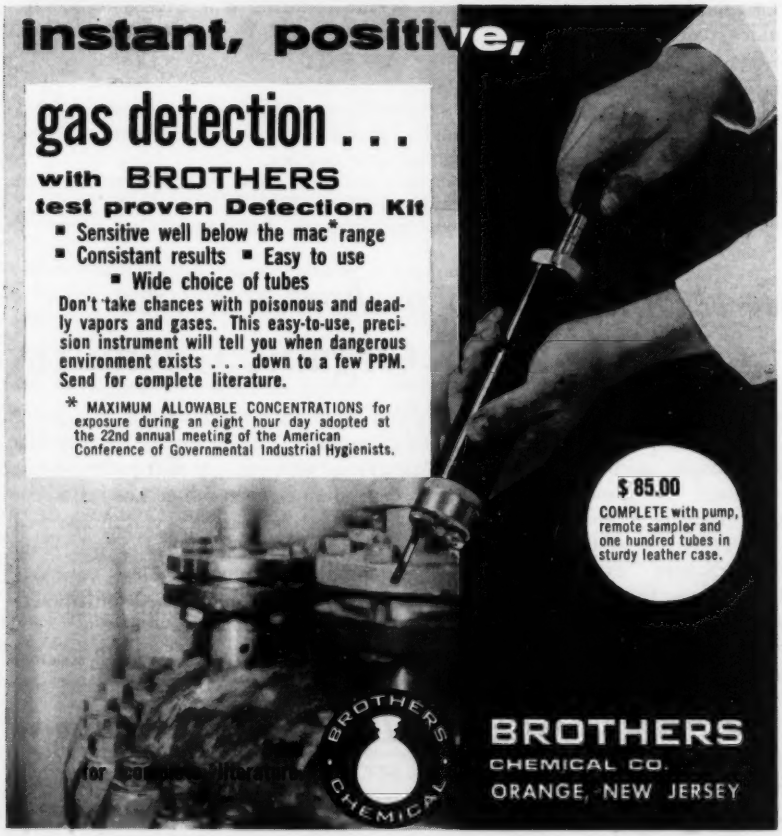

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lacks the balance that would have been provided by a concern with current research in the field.

WALTER J. MOORE
Indiana University
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Nutritional Evaluation of Food Processing

Edited by *Robert S. Harris*, Massachusetts Institute of Technology, Cambridge, and *Harry von Loesecke*, formerly Agricultural Research Service, U. S. Department of Agriculture. John Wiley & Sons, Inc., New York, 1960. xviii + 612 pp. Figs. and tables. 16 × 23.5 cm. $12.

This book represents the efforts of 33 recognized authorities in the fields of nutrition biochemistry and food technology to evaluate the effects of processing upon the nutritional value of foods as they proceed from "garden to gullet." The varied material of this book is presented in 13 chapters, each chapter followed by a list of references. The following topics give an appreciation of the range of areas covered: influences of genetics and of agricultural practices on the composition of foods; relation of harvesting and handling practices of unprocessed foods to their composition; effects of commercial processing on the composition of fruits and vegetables; effects of commercial processing of milk and milk products on their composition; effects of commercial processing of cereals on their composition; effects of commercial processing of oilseeds and oil on their composition; influence of commercial processing on the composition of meat, poultry, and fish products; relation of packaging materials to maintenance of nutritive value; effect of commercial storage on the nutritive value of processed foods; losses in nutrients during large-scale preparation for direct feeding; losses in nutrients during home preparation of foods; methods of increasing the nutritive value of foods; factors affecting utilization of food nutrients by the normal organism. An index is arranged by both author and subject sequence.

The book contains some shortcomings often associated with collected work. For example, there is some overlapping in some areas and while some subjects are treated with accuracy and provide up-to-date information, others are not so well prepared.

To our knowledge, however, this is the first published accumulation of knowledge concerning the various nutritional aspects of food processing. It will serve as a useful text for the student of food technology, home economics, or nutrition and can be of great value to both the commercial producer or manufacturer and to the consumer.

IRVING S. FAGERSON
University of Massachusetts
Amherst

(*Continued on page A370*)

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by Harry H. Sisler and Jay J. Stewart, Research and Development, E. I. duPont de Nemours & Co., Inc., Wilmington

Spring, 1961

A SHORT COURSE OF ORGANIC CHEMISTRY

by John Edward Leffler, Associate Professor of Chemistry, Florida State University

This text introduces basic concepts, language, and symbolism of organic chemistry for students who are not majoring in the subject. Special reference is given to the role of organic chemistry in industry, its relation to other aspects of our culture, and its place in everyday life. Chapters on special types, showing practical application of concepts and information, are provided.

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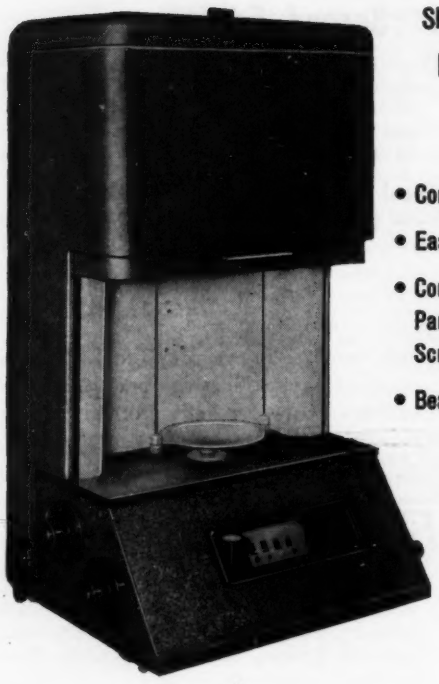

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Encyclopedia of Chemical Technology. Second Supplement Volume

Edited by *Raymond E. Kirk* and *Donald F. Othmer*, both of Polytechnic Institute of Brooklyn, New York. 2nd supplement volume, edited by *Anthony Standen*. Interscience Encyclopedia, Inc., New York, 1960. xv + 970 pp. Figs. and tables. 20 × 27 cm. $25.

It takes a good book like this to jolt the reader to realize that there has been such a tremendous amount of new developments since the appearance of the first 15 volumes of the Encyclopedia of Chemical Technology in 1957. This second supplement to the Encyclopedia of Chemical Technology, like the first supplement, consists of 59 independent articles arranged alphabetically. Cross references are made to articles in the original 15 volumes of the Encyclopedia and to the first supplement.

The index covers this volume alone and should be consulted together with the index to the first supplement and to the index to the original set, in Volume 15. An integrated list of the articles in the first 15 volumes, together with the two supplements, appears at the end of this volume.

This supplement was edited by Dr. Anthony Standen who should be commended for the outstanding job.

There are 59 major subjects covered in this supplement. These are all covered in the extremely high quality consistent with the first 15 volumes. Although each article is very well presented, the ones which were of greatest interest to this reviewer included the articles on Acetylene, Acetylenic Alcohols, Borazines, Boron Compounds, Electric Cells, Ceramics, Chemical Coding, Chitin, Cryogenics, Diffusion Separation, Electrodeposition, Epoxidation, Free Radicals, Fuel Cells, Gas Chromatography, Magnetic Materials, Synthetic Mica, Nonionic Surfactants, Oxo Process, Polycarbonates, Polymethylbenzenes, Polyoxetanes, Polypropylene, Polyvinylpyrrolidone, Solid State, Solions, Stereoregular Polymers, Thermoelectric Power, Ultraviolet Absorbers, and Unsaturated Polyester Resins.

No library, including the high school libraries, should be without the entire set of Encyclopedia of Technology. This certainly includes the first and second Supplement Volumes.

JOHN J. MCKETTA
University of Texas
Austin

Statistical Theory and Methodology in Science and Engineering

K. A. Brownlee, University of Chicago, Chicago, Illinois. John Wiley & Sons, Inc., New York, 1960. xv + 570 pp. Figs. and tables. 16 × 23.5 cm. $16.75.

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(*Continued on page A372*)

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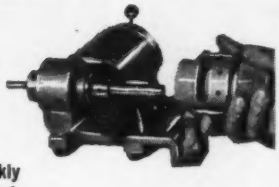

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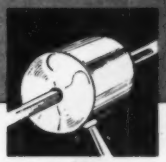

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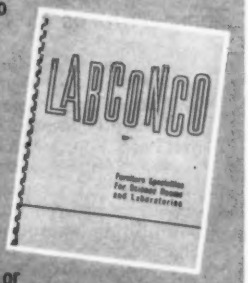

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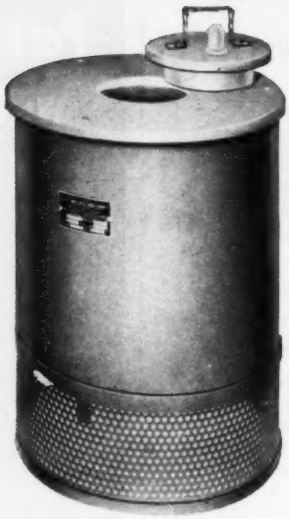

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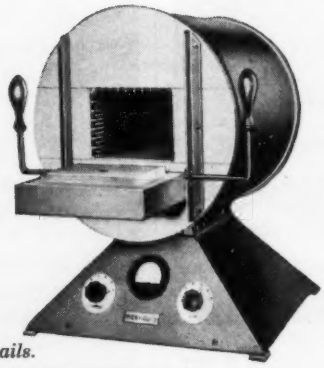

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BOOK REVIEWS

many (including this reviewer) to try statistically designed experiments. With the publication of this new work, Professor Brownlee has again produced a book appropriate to the times. In contrast to the earlier book, this one bristles with proofs and mathematical demonstrations. The level is "elementary" and most steps involve only simple algebra, but the reader will soon find himself in that sea of symbolism so necessary in any detailed exposition of the mathematical structure of statistics.

The development of the subject follows the order: introductory ideas, binomial, hypergeometric, Poisson, chi-square distributions, control charts, nonparametric tests, parametric tests for means and variances, analysis of variance, and regression. One- through four-way analyses of variance are considered in great detail as are completely and partially hierarchical (nested) designs. Particular attention is paid to the expectations of mean squares for various models. Regression is also treated in more than usual detail.

A splendid feature of this book is the use of many real examples taken from the literature of chemistry and physics both for expository purposes and as problems. Answers to about one-third of the problems are given. Both general and specific references are provided for further study.

Despite the fact that this book is designed to be a text (for students majoring in either statistics or an experimental science), the subjects are covered in such detail that it should prove useful for self-study. Experimental designs are not covered in any depth, but topics in this field are listed and pertinent references are given. An appendix includes 10 commonly used tables. The typography and figures are excellent. The author has succeeded in his objective of providing the means for obtaining both facility and self-confidence in the use of statistical methods.

LLOYD S. NELSON
General Electric Lamp Division
Cleveland, Ohio

Gmelins Handbuch der Anorganischen Chemie. 8 Auflage. System Nummer 33, Cadmium, erganzungsband

Edited by the Gmelin Institute under the direction of *E. H. B. Pietsch*. 8th edition. Verlag Chemie, GMBH., Weinheim, Bergstrasse, 1959. 802 pp. Figs. and tables. 17.5 × 25.5 cm. Paperbound. $121.

This supplement represents a collection of research results from 1924 to the end of 1949. There was a need for a supplement to the earlier Gmelin volume dealing with cadmium as evidenced by the extent of the literature surveyed by this new work. The magnitude of this supplement makes it virtually impossible to evaluate critically the volume of its entirety. However, the following will give the

(*Continued on page A374*)

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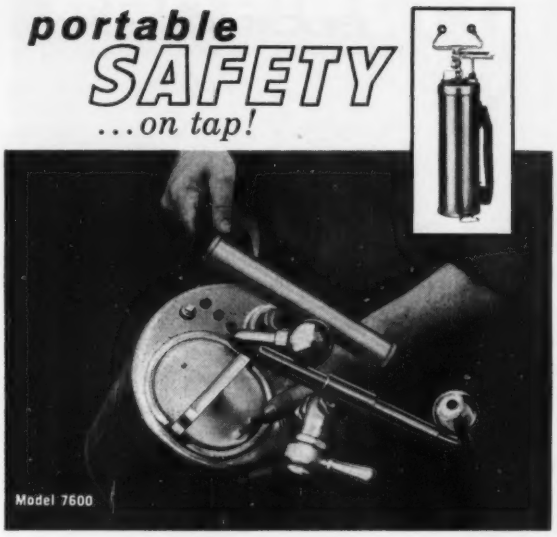

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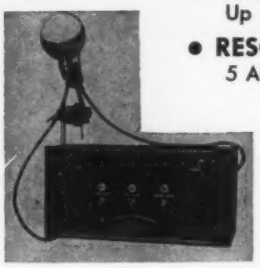

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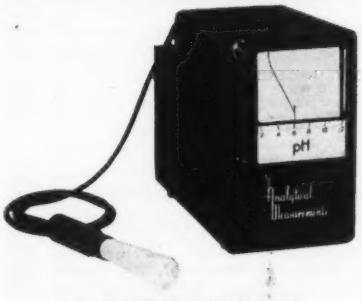

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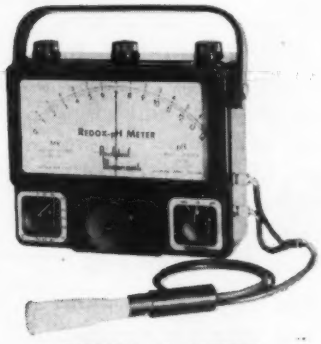

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prospective purchaser some idea of the topics treated.

A small section is devoted to the preparations (primarily industrial) of the pure element by distillation, concentration, electrolysis, and chemical reaction. The physical properties are thoroughly treated in a large section (140 pages) of this 802-page supplementary volume. This section contains discussion of the crystallographic, mechanical, thermal, optical, magnetic and electrical properties of cadmium.

The electro-chemical behavior section (127 pages) contains, in addition to standard potential data, subjects of current interest such as the Cadmium-Nickel battery (up to 1958) and the polarographic behavior of cadmium in aqueous and non-aqueous media. Thirty eight pages are devoted to the electrolytic deposition of cadmium from a variety of baths.

Reactions of elemental and ionic cadmium have been surveyed in great detail. The ionic reactions are treated with a special view toward those reactions of analytical importance. Topics of current interest, such as the reactions of the cadmium ion with organic compounds are extensively examined.

A section on alloys composes 60 pages, with a great deal of this space devoted to cadmium-zinc alloys. Every conceivable compound and complex has been covered in the section devoted to cadmium compounds.

This extensive source of information should serve as an excellent guide for anyone starting a literature search for information concerning this element.

THEODORE R. WILLIAMS
The College of Wooster
Wooster, Ohio

A Short History of Chemistry

J. R. Partington, University of London, England. 3rd ed. Harper Torchbook, Harper & Brothers, New York, 1960. xiii + 415 pp. 127 figs. 20 × 13.5 cm. Paperbound. $1.95.

The first edition of this book appeared in 1937, when it was given a favorable review in THIS JOURNAL (15, 198 (1938)) by the late Tenney L. Davis. An essentially unchanged second edition appeared in 1948, a third edition in 1957. The latter, from which this paperback edition is taken, is little changed from the first except for small expansions of the chapters dealing with physical chemistry and atomic structure. Since the book is a sound and concise treatment of the growth of chemistry to the twentieth century, it is good to have it available in a well-printed but inexpensive reprint.

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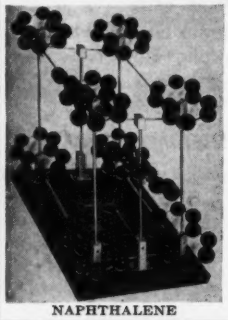

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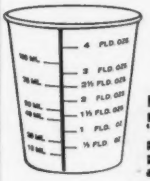

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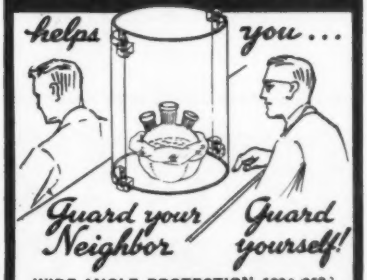

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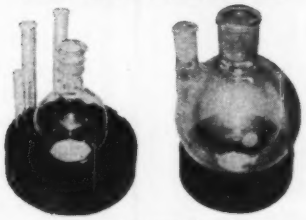

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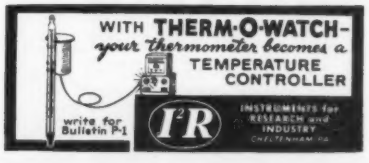

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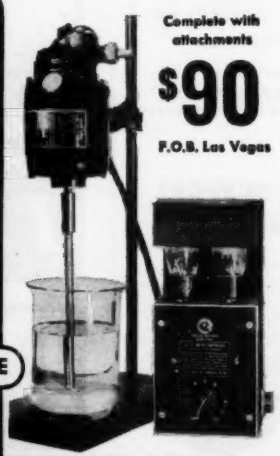

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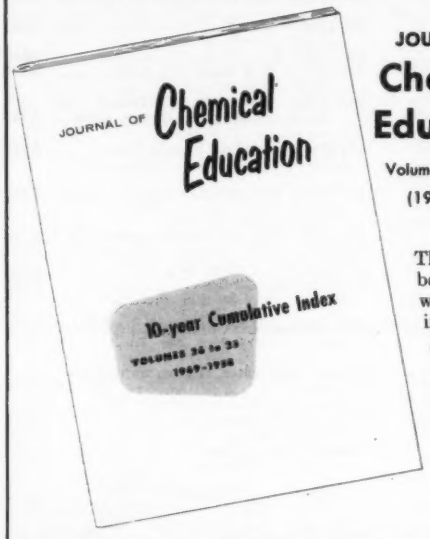

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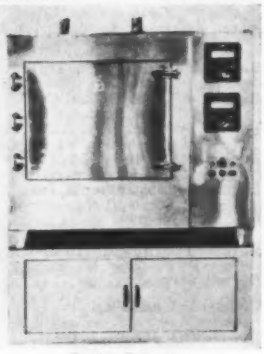

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